Supporting Information for

Iridium-Catalyzed Intramolecular Asymmetric Allylic Etherification of Salicylic Acid Derivatives with Chiral-Bridged Biphenyl Phosphoramidite Ligands

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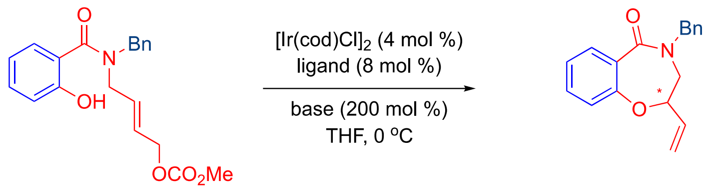
1. General considerations

Unless otherwise stated, all syntheses and manipulations of air- and moisture-sensitive materials were carried out in a nitrogen-filled glovebox or under nitrogen atmosphere using standard Schlenk techniques. All glassware was oven-dried immediately prior to use. All solvents were freshly distilled and degassed according to standard methods. Reactions were magnetically stirred and monitored by analytical thin-layer chromatography (TLC). TLC was performed on Merck silica gel 60 F254 TLC glass plates and visualized by exposure to ultraviolet light. Organic solutions were concentrated by rotary evaporation at 20 – 45 °C.

All chemicals and reagents available from commercial sources were directly used without further purification. Chromatographic purification of products was accomplished using forced-flow chromatography on silica gel (200 – 300 mesh). ^{1}H, ^{19}F, and ^{13}C NMR spectra were recorded on a Bruker Ascend 400 MHz spectrometer at ambient temperature. High-resolution mass spectra (HRMS) were obtained with Shimazu LC-20AT mass spectrometer. Optical rotations were measured on SGW®-5 automatic polarimeter. Enantiomeric excesses (ee values) of the products were determined by chiral HPLC analysis using an Aglient HP 1200 instrument (n-hexane/2-propanol as eluent) with a Chiralpak IF-3 or IA-3 Column. The phosphoramidite ligands **L1 – L8** were prepared according to the reported procedures.

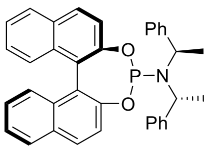
2. Table S1 Optimization of Reaction Conditions[a]



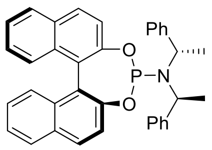
1a **2a**

entry	solvent	ligand	base	t[°C]	T[h]	yield[%][b]	ee[%][c]
1	THF	**L1**	DBU	0	10	91	90
2	THF	**L2**	DBU	0	10	92	-90
3	THF	**L3**	DBU	0	20	trace	\
4	THF	**L4**	DBU	0	8	94	92
5	THF	**L5**	DBU	0	20	32	-51
6	THF	**L6**	DBU	0	20	37	-89
7	THF	**L7**	DBU	0	8	96	93
8	THF	**L8**	DBU	0	20	63	87
9	THF	**L7**	K_3PO_4	0	16	95	88
10	THF	**L7**	DABCO	0	16	93	89
11	THF	**L7**	Et_3N	0	16	84	88
12	THF	**L7**	Cs_2CO_3	0	16	67	84
13	THF	**L7**	\	0	16	61	84
14	DME	**L7**	DBU	0	22	76	91
15	dioxane	**L7**	DBU	0	22	79	87
16	DCE	**L7**	DBU	0	22	94	79
17	DCM	**L7**	DBU	0	22	87	73
18	MTBE	**L7**	DBU	0	22	94	78
19	PhMe	**L7**	DBU	0	22	91	89
20	THF	**L7**	DBU	-10	8	96	92
21	THF	**L7**	DBU	10	2	94	92
22	THF	**L1**	DBU	rt	0.5	92	90
23	THF	**L7**	DBU	rt	10 min	94	92
24	THF	**L7**	DBU	40	10 min	92	91
25	THF	**L7**	DBU	50	10 min	90	85
26[d]	THF	**L7**	DBU	rt	10 min	96	93
27[e]	THF	**L7**	DBU	rt	10 min	30	92

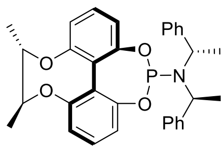
[a] Conditions: $[Ir(cod)Cl]_2$ (4 mol %), ligand (8 mol %), base (0.2 mmol), and **1a** (0.1 mmol) in solvent (2.0 mL). [b] Isolated yields. [c] Determined by chiral HPLC analysis. [d] 2 mol % of Ir catalyst was used. [e] 1 mol % of Ir catalyst was used.



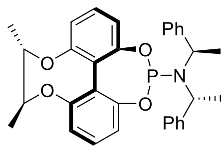
L1 (***R**$_a$**, R, R***)



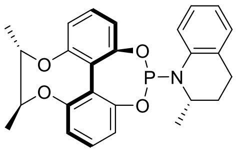
L2 (***S**$_a$**, S, S***)



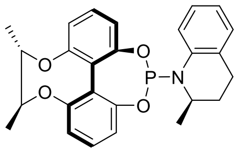
L3 (***S, S, R**$_a$**, S, S***)



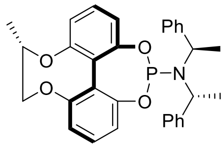
L4 (***S, S, R**$_a$**, R, R***)



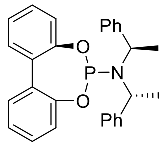
L5 (***S, S, R**$_a$**, S***)



L6 (***S, S, R**$_a$**, R***)



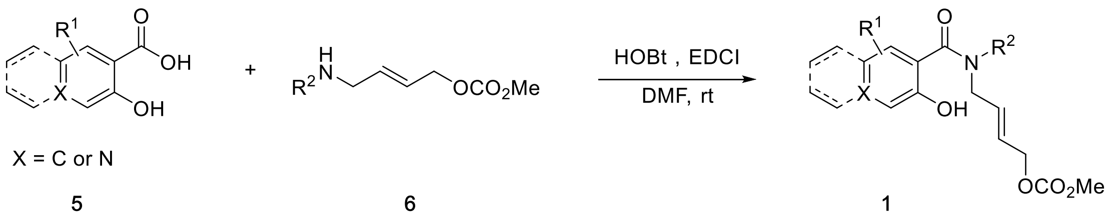
L7 (***S, R**$_a$**, R, R***)



L8 (***R, R***)

3. Experimental Procedures

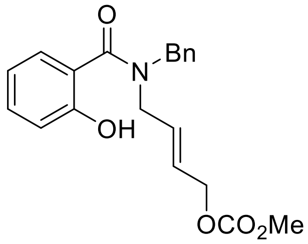
3.1 General Procedure for the Synthesis of Salicylic Acid Derivatives 1



5 6 1

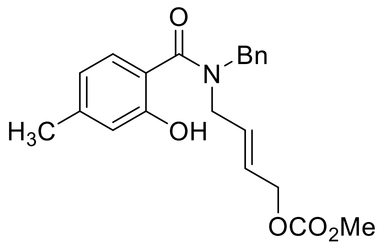
To a solution of substituted salicylic acids **5** (2 mmol, 1.0 equiv.) in DMF (10 mL), 1-hydroxybenzotrizole (HOBt) (297 mg, 2.2 mmol, 1.1 equiv.) and *N*-(3-dimethylaminopropyl)-*N′*-ethylcarbodiimide hydrochloride (EDC·HCl) (422 mg, 2.2 mmol, equiv.) were added. This mixture was stirred for 30 minutes at room temperature, then compounds **6** (2 mmol, 1.0 equiv.) was added. After the reaction was complete (monitored by TLC), the crude reaction mixture was diluted with EtOAc (20 mL) and washed with water (10 mL x 3) and brine (15 mL x 3). The combined organic layers were dried over Na_2SO_4. Afterwards, the solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography (petroleum/EtOAc = 3 : 1) to afford the desired compounds **1**.

(*E*)-4-(*N*-benzyl-2-hydroxybenzamido)but-2-en-1-yl methyl carbonate (1a)



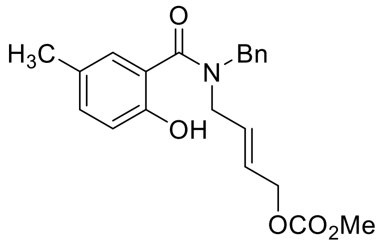
Yellow oil, 0.67 g, 95% yield; ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.78 (s, 1H), 7.47 – 7.26 (m, 7H), 7.05 (d, *J* = 8.2 Hz, 1H), 6.80 (t, *J* = 7.4 Hz, 1H), 5.91 (m, 1H), 5.83 – 5.65 (m, 1H), 4.76 (s, 2H), 4.69 (d, *J* = 5.2 Hz, 2H), 4.09 (d, *J* = 4.8 Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 172.42, 159.09, 155.52, 136.13, 132.93, 129.39, 128.95, 127.77, 127.55, 127.43, 118.65, 118.28, 118.19, 117.06, 67.29, 54.92. HRMS (ESI) calcd for $C_{20}H_{21}NO_5$ $[M+H]^+$: 356.1493, Found: 356.1485.

(*E*)-4-(*N*-benzyl-2-hydroxy-4-methylbenzamido)but-2-en-1-yl methyl carbonate (1b)



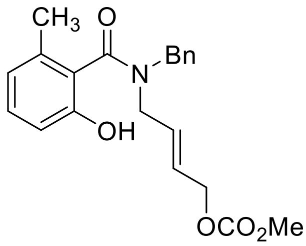
Yellow oil, 0.63 g, 85% yield; ^{1}H NMR (400 MHz, CDCl$_3$) δ 10.01 (s, 1H), 7.43 – 7.27 (m, 5H), 7.21 (d, *J* = 8.0 Hz, 1H), 6.85 (s, 1H), 6.60 (d, *J* = 7.9 Hz, 1H), 5.91 (m, 1H), 5.83 – 5.70 (m, 1H), 4.75 (s, 2H), 4.69 (d, *J* = 5.5 Hz, 2H), 4.07 (d, *J* = 5.1 Hz, 2H), 3.83 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 172.64, 159.39, 155.53, 143.93, 136.24, 129.52, 128.93, 127.71, 127.43, 127.36, 119.62, 118.46, 114.04, 67.33, 54.92, 21.54. HRMS (ESI) calcd for $C_{21}H_{23}NO_5$ $[M+H]^+$: 370.1649, Found: 370.1643.

(*E*)-4-(*N*-benzyl-2-hydroxy-5-methylbenzamido)but-2-en-1-yl methyl carbonate (1c)



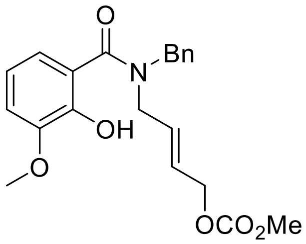
Yellow oil, 0.61 g, 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (m, 5H), 7.20 – 7.09 (m, 2H), 6.94 (d, *J* = 8.4 Hz, 1H), 5.96 – 5.85 (m, 1H), 5.82 – 5.71 (m, 1H), 4.75 (s, 2H), 4.69 (d, *J* = 5.5 Hz, 2H), 4.08 (d, *J* = 5.0 Hz, 2H), 3.83 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.41, 156.24, 155.54, 136.29, 133.47, 129.63, 128.89, 127.89, 127.72, 127.57, 127.44, 117.82, 117.33, 67.33, 54.91, 20.42. HRMS (ESI) calcd for $C_{21}H_{23}NO_5$ $[M+H]^+$: 370.1661, Found: 370.1642.

(*E*)-4-(*N*-benzyl-2-hydroxy-6-methylbenzamido)but-2-en-1-yl methyl carbonate (1d)



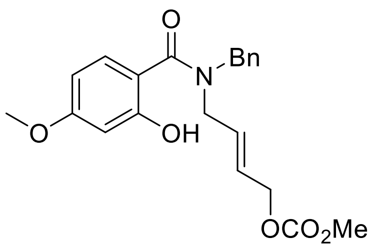
Yellow oil, 0.63 g, 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.27 (m, 5H), 7.21 (d, *J* = 8.0 Hz, 1H), 6.85 (s, 1H), 6.60 (d, *J* = 7.8 Hz, 1H), 5.90 (m, 1H), 5.77 (m, 1H), 4.75 (s, 2H), 4.69 (m, 2H), 4.08 (d, *J* = 8.0 Hz, 2H), 3.83 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.44, 155.57, 152.88, 135.48, 129.98, 128.69, 128.36, 127.66, 122.00, 114.21, 67.41, 54.90, 19.14. HRMS (ESI) calcd for $C_{21}H_{23}NO_5$ $[M+H]^+$: 370.1661, Found: 370.1642.

(*E*)-4-(*N*-benzyl-2-hydroxy-3-methoxybenzamido)but-2-en-1-yl methyl carbonate (1e)



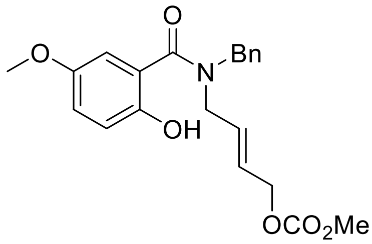
Yellow oil, 0.72 g, 93% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (m, 5H), 6.92 (d, *J* = 3.7 Hz, 2H), 6.86 (d, *J* = 7.1 Hz, 1H), 5.82 (m, 1H), 5.72 (m, 1H), 4.68 (s, 2H), 4.65 (d, J = 4.0 Hz, 2H), 3.99 (d, J = 4.0 Hz, 2H), 3.92 (s, 3H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.23, 155.54, 147.60, 144.55, 136.49, 129.92, 128.74, 127.69, 127.56, 126.90, 120.91, 119.65, 119.57, 112.47, 67.47, 56.19, 54.89, 53.44. HRMS (ESI) calcd for $C_{21}H_{23}NO_6$ $[M+H]^+$: 386.1610, Found: 386.1588.

(*E*)-4-(*N*-benzyl-2-hydroxy-4-methoxybenzamido)but-2-en-1-yl methyl carbonate (1f)



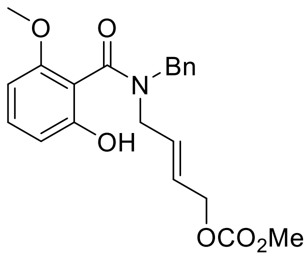
Yellow oil, 0.56g, 73% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (m, 6H), 6.55 (d, *J* = 2.3 Hz, 1H), 6.33 (dd, *J* = 8.7, 2.1 Hz, 1H), 5.92 (m, 1H), 5.85 – 5.71 (m, 1H), 4.74 (s, 2H), 4.69 (d, *J* = 8.0 Hz, 2H), 4.08 (d, *J* = 4.0 Hz, 2H), 3.83 (s, 3H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.85, 163.52, 162.36, 155.52, 136.29, 129.58, 128.94, 127.70, 127.42, 108.94, 105.95, 102.06, 67.33, 55.37, 54.90, 50.79, 48.76. HRMS (ESI) calcd for $C_{21}H_{23}NO_6$ $[M+H]^+$: 386.1610, Found: 386.1589.

(*E*)-4-(*N*-benzyl-2-hydroxy-5-methoxybenzamido)but-2-en-1-yl methyl carbonate (1g)



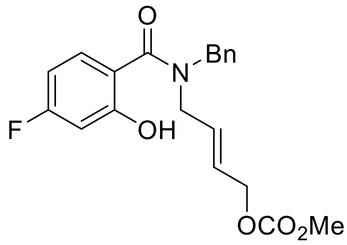
Yellow oil, 0.67 g, 87% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.41 – 8.94 (m, 1H), 7.37 (m, 5H), 6.93 (m, 3H), 6.11 – 5.71 (m, 2H), 4.76 (s, 2H), 4.70 (d, *J* = 4.0 Hz, 2H), 4.10 (m, 2H), 3.83 (s, 3H), 3.51 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.20, 155.54, 152.50, 151.77, 136.29, 129.45, 128.98, 127.74, 127.51, 127.24, 119.87, 118.94, 117.40, 111.21, 67.29, 55.52, 54.90, 48.50. HRMS (ESI) calcd for $C_{21}H_{23}NO_6$ $[M+H]^+$: 386.1610, Found: 386.1589.

(*E*)-4-(*N*-benzyl-2-hydroxy-6-methoxybenzamido)but-2-en-1-yl methyl carbonate (1h)



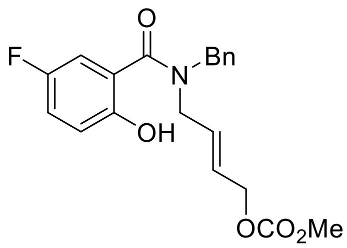
Brown oil, 0.67 g, 87% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.26 (m, 6H), 6.57 (d, *J* = 8.0 Hz, 1H), 6.43 (d, *J* = 7.4 Hz, 1H), 5.80 (m, 1H), 5.74 – 5.45 (m, 1H), 4.86 – 4.21 (m, 4H), 3.79 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.86, 156.43, 156.35, 156.33, 156.01, 155.96, 155.91, 155.88, 155.62, 155.57, 136.55, 136.38, 136.33, 131.14, 131.11, 130.47, 129.63, 128.57, 127.89, 127.84, 127.59, 127.25, 127.22, 125.83, 111.70, 111.60, 110.12, 102.30, 67.85, 67.34, 55.55, 54.85, 52.15, 49.62, 47.15, 44.78. HRMS (ESI) calcd for $C_{21}H_{23}NO_6$ $[M+H]^+$: 386.1610, Found: 386.1589.

(E)-4-(N-benzyl-4-fluoro-2-hydroxybenzamido)but-2-en-1-yl methyl carbonate (1i)



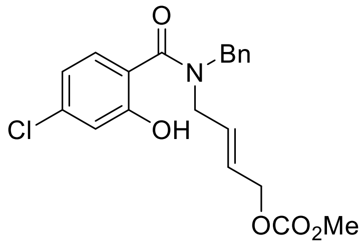
Brown oil, 0.64 g, 86% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.46 (s, 1H), 7.47 – 7.28 (m, 6H), 6.73 (m, 1H), 6.51 (m, 1H), 5.91 (m, 1H), 5.83 – 5.73 (m, 1H), 4.74 (s, 2H), 4.69 (d, J = 8.0 Hz, 2H), 4.07 (d, J = 4.9 Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.99, 162.95 (d, J = 221.0 Hz), 161.71, 155.52, 135.94, 129.16 (dd, J = 15.8, 12.0 Hz), 127.77 (d, J = 16.6 Hz), 127.37, 113.19, 106.30, 106.08, 105.37, 105.14, 67.23, 54.92, 50.68, 48.70. ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.28. HRMS (ESI) calcd for $C_{20}H_{20}FNO_5$ $[M+H]^+$: 374.1409, Found: 374.1390.

(E)-4-(N-benzyl-5-fluoro-2-hydroxybenzamido)but-2-en-1-yl methyl carbonate (1j)



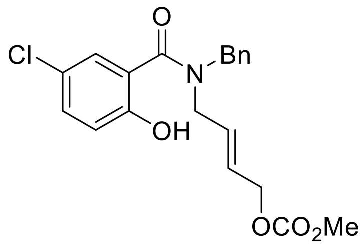
Brown oil, 0.64 g, 86% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.28 (m, 5H), 7.03 (m, 3H), 5.90 (m, 1H), 5.86 (m, 1H), 4.73 (s, 2H), 4.69 (d, J = 4.0 Hz, 2H), 4.06 (d, J = 4.9 Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.11, 155.52, 154.95 (d, J = 237.0 Hz), 154.57, 135.80, 129.05 (d, J = 8.9 Hz), 127.91, 127.61 (d, J = 23.4 Hz), 119.80, 119.57, 119.23 (d, J = 7.6 Hz), 117.92, 113.54, 113.30, 67.19, 54.93, 50.41, 48.58. ^{19}F NMR (376 MHz, $CDCl_3$) δ -124.04. HRMS (ESI) calcd for $C_{20}H_{20}FNO_5$ $[M+H]^+$: 374.1409, Found: 374.1392.

(*E*)-4-(*N*-benzyl-4-chloro-2-hydroxybenzamido)but-2-en-1-yl methyl carbonate (1k)



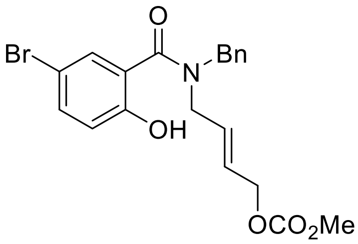
Brown oil, 0.57 g, 73% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.13 (s, 1H), 7.46 – 7.25 (m, 6H), 7.03 (d, *J* = 1.4 Hz, 1H), 6.78 (d, *J* = 8.1 Hz, 1H), 5.88 (m, 1H), 5.83 – 5.70 (m, 1H), 4.72 (s, 2H), 4.68 (d, *J* = 8.0 Hz, 2H), 4.06 (d, *J* = 4.8 Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.70, 159.81, 155.52, 138.37, 135.87, 129.08, 129.01, 128.37, 127.87, 127.71, 127.41, 119.12, 118.35, 115.87, 115.83, 67.22, 54.93, 50.67, 48.62. HRMS (ESI) calcd for $C_{20}H_{20}ClNO_5$ $[M+H]^+$: 390.1114, Found: 390.1094.

(*E*)-4-(*N*-benzyl-5-chloro-2-hydroxybenzamido)but-2-en-1-yl methyl carbonate (1l)



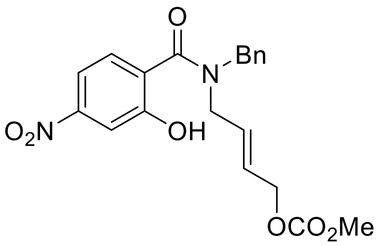
Brown oil, 0.5 g, 64% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.60 (s, 1H), 7.46 – 7.23 (m, 7H), 6.97 (d, *J* = 8.5 Hz, 1H), 5.89 (m, 1H), 5.79 (m, 1H), 4.73 (s, 2H), 4.69 (d, *J* = 4.0 Hz, 2H), 4.06 (d, *J* = 5.2 Hz, 2H), 3.91 – 3.66 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.01, 157.15, 155.52, 135.79, 132.60, 129.02, 129.00, 127.92, 127.85, 127.58, 127.04, 123.58, 119.53, 118.68, 67.18, 54.94, 50.52, 49.00. HRMS (ESI) calcd for $C_{20}H_{20}ClNO_5$ $[M+H]^+$: 390.1114, Found: 390.1093.

(*E*)-4-(*N*-benzyl-5-bromo-2-hydroxybenzamido)but-2-en-1-yl methyl carbonate (1m)



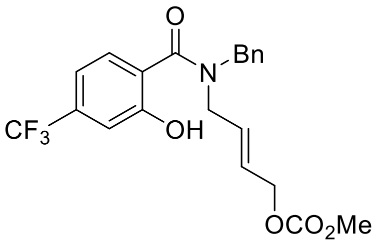
Pale yellow oil, 0.81 g, 93% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 (s, 1H), 7.32 (m, 7H), 6.83 (d, *J* = 8.7 Hz, 1H), 5.88 – 5.79 (m, 1H), 5.78 – 5.68 (m, 1H), 4.69 (s, 2H), 4.65 (d, *J* = 8.0 Hz, 2H), 4.01 (m, 2H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.60, 156.21, 155.53, 135.87, 134.86, 129.94, 129.10, 128.92, 127.84, 127.70, 120.91, 119.61, 110.73, 67.23, 60.45, 54.92, 48.59. HRMS (ESI) calcd for $C_{20}H_{20}BrNO_5$ $[M+H]^+$: 434.0609, Found: 434.0589.

(*E*)-4-(*N*-benzyl-2-hydroxy-4-nitrobenzamido)but-2-en-1-yl methyl carbonate (1n)



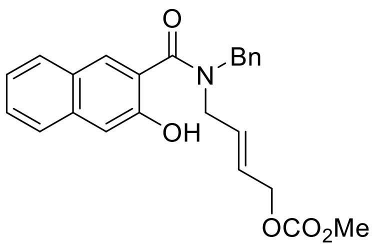
Brown oil, 0.74 g, 92% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 1.8 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.47 – 7.25 (m, 6H), 5.84 (m, 1H), 5.77 (m, 1H), 4.70 (s, 2H), 4.67 (d, *J* = 4.0 Hz, 2H), 4.02 (d, *J* = 3.7 Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.11, 157.71, 155.54, 149.86, 135.44, 129.04, 128.63, 128.10, 128.04, 127.93, 113.87, 112.84, 67.15, 54.98. HRMS (ESI) calcd for $C_{20}H_{20}N_2O_7$ $[M+H]^+$: 401.1355, Found: 401.1335.

(*E*)-4-(*N*-benzyl-2-hydroxy-4-(trifluoromethyl)benzamido)but-2-en-1-yl methyl carbonate (1o)



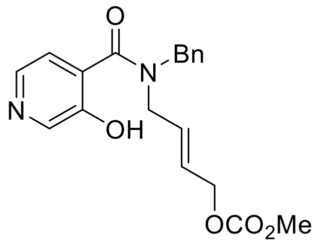
Pale yellow oil, 0.8 g, 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (s, 1H), 7.48 – 7.36 (m, 4H), 7.28 (d, *J* = 9.3 Hz, 3H), 7.06 (d, *J* = 7.3 Hz, 1H), 5.88 (m, 1H), 5.77 (m, 1H), 4.73 (s, 2H), 4.68 (d, *J* = 8.0 Hz, 2H), 4.06 (m, 2H), 3.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.97, 158.26, 155.53, 135.68, 134.35, 134.02, 129.04, 128.88, 127.95, 127.93, 127.81, 124.65, 121.94, 121.18, 115.33 (dd, *J* = 25.2, 3.7 Hz), 67.20, 58.45, 54.96, 53.43. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.51. HRMS (ESI) calcd for $C_{21}H_{20}F_3NO_5$ $[M+H]^+$: 424.1378, Found: 424.1357.

(*E*)-4-(*N*-benzyl-3-hydroxy-2-naphthamido)but-2-en-1-yl methyl carbonate (1p)



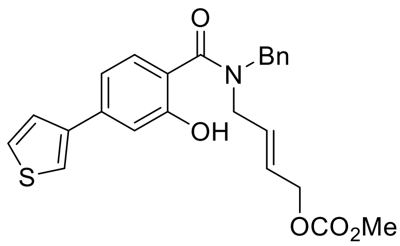
Pale yellow oil, 0.75 g, 92% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.50 – 7.29 (m, 9H), 5.93 (m, 1H), 5.85 – 5.76 (m, 1H), 4.80 (s, 2H), 4.70 (d, *J* = 5.3 Hz, 2H), 4.13 (m, 2H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.82, 155.56, 153.80, 136.14, 135.86, 129.43, 128.96, 128.44, 127.99, 127.82, 127.57, 126.96, 126.32, 123.99, 120.72, 112.17, 67.30, 54.93. HRMS (ESI) calcd for $C_{24}H_{23}NO_5$ $[M+H]^+$: 406.1665, Found: 406.1642.

(*E*)-4-(*N*-benzyl-3-hydroxyisonicotinamido)but-2-en-1-yl methyl carbonate (1q)



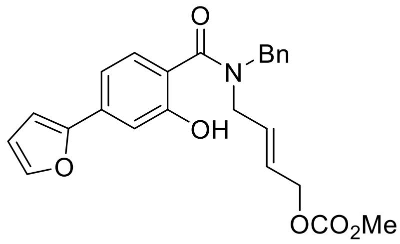
Yellow oil, 0.67 g, 87% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.13 (s, 1H), 7.45 – 7.23 (m, 6H), 5.76 (m, 2H), 4.66 (s, 2H), 4.64 (m, 2H), 4.04 (m, 2H), 3.83 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 168.25, 155.49, 150.99, 139.67, 138.55, 135.84, 130.62, 128.80, 127.78, 121.94, 67.18, 60.43, 54.89, 53.49. HRMS (ESI) calcd for $C_{19}H_{20}N_2O_5$ $[M+H]^+$: 357.1455, Found: 357.1438.

(*E*)-4-(*N*-benzyl-2-hydroxy-4-(thiophen-3-yl)benzamido)but-2-en-1-yl methyl carbonate (1r)



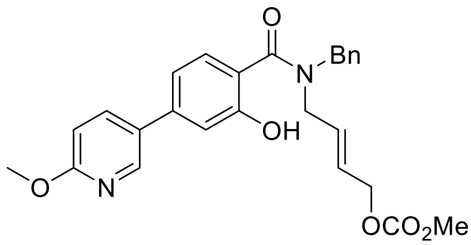
Yellow oil, 0.75 g, 86% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.17 (s, 1H), 7.53 (s, 1H), 7.45 – 7.29 (m, 9H), 7.04 (d, *J* = 7.9 Hz, 1H), 5.93 (m, 1H), 5.79 (m, 1H), 4.78 (s, 2H), 4.71 (d, *J* = 5.1 Hz, 2H), 4.11 (d, *J* = 4.4 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.34, 159.85, 155.53, 140.96, 140.25, 136.15, 129.38, 128.99, 128.02, 127.78, 127.58, 126.52, 126.09, 121.79, 116.74, 115.58, 115.34, 67.31, 54.93. HRMS (ESI) calcd for $C_{24}H_{23}NO_5S$ $[M+H]^+$: 438.1386, Found: 438.1361.

(*E*)-4-(*N*-benzyl-4-(furan-2-yl)-2-hydroxybenzamido)but-2-en-1-yl methyl carbonate (1s)



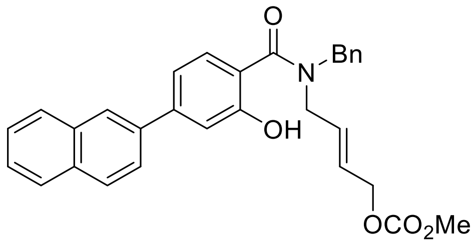
Brown oil, 0.78 g, 93% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.37 (m, 7H), 7.11 (d, *J* = 8.1 Hz, 1H), 6.73 (s, 1H), 6.50 (s, 1H), 5.93 (m, 1H), 5.79 (m, 1H), 4.77 (s, 2H), 4.70 (d, *J* = 5.2 Hz, 2H), 4.10 (d, *J* = 4.7 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.31, 159.83, 155.53, 152.71, 143.00, 136.11, 135.05, 129.35, 128.98, 128.03, 127.78, 127.61, 127.40, 115.31, 114.07, 112.80, 111.90, 107.15, 67.29, 54.93. HRMS (ESI) calcd for $C_{24}H_{23}NO_6$ $[M+H]^+$: 422.1614, Found: 422.1591.

(*E*)-4-(*N*-benzyl-2-hydroxy-4-(6-methoxypyridin-3-yl)benzamido)but-2-en-1-yl methyl carbonate (1t)



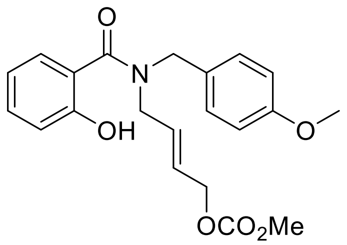
Yellow oil, 0.8 g, 87% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.43 – 7.28 (m, 6H), 7.19 (s, 1H), 6.96 (d, *J* = 7.7 Hz, 1H), 6.82 (d, *J* = 8.5 Hz, 1H), 5.92 (m, 1H), 5.83 – 5.69 (m, 1H), 4.77 (s, 2H), 4.69 (d, *J* = 5.5 Hz, 2H), 4.09 (d, *J* = 5.1 Hz, 2H), 3.99 (s, 3H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.12, 164.02, 159.39, 159.32, 155.53, 144.98, 142.26, 137.40, 136.09, 129.34, 128.98, 128.69, 128.18, 127.79, 127.56, 127.43, 116.91, 115.71, 110.99, 67.97, 67.31, 54.94, 53.75. HRMS (ESI) calcd for $C_{26}H_{26}N_2O_6$ $[M+H]^+$: 463.1882, Found: 463.1853.

(*E*)-4-(*N*-benzyl-2-hydroxy-4-(naphthalen-2-yl)benzamido)but-2-en-1-yl methyl carbonate (1u)



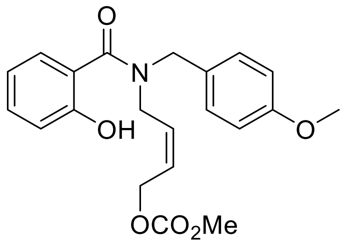
Yellow oil, 0.87 g, 90% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (m, 3H), 7.64 – 7.31 (m, 12H), 7.22 (s, 1H), 6.96 (d, *J* = 7.7 Hz, 1H), 5.96 (m, 1H), 5.82 (m, 1H), 4.84 (s, 2H), 4.72 (d, *J* = 4.5 Hz, 2H), 4.17 (d, *J* = 3.4 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.30, 158.96, 155.56, 145.69, 138.98, 136.22, 133.77, 131.17, 129.49, 128.99, 128.33, 128.19, 127.90, 127.80, 127.56, 127.37, 126.71, 126.25, 125.93, 125.78, 125.31, 120.65, 119.63, 116.15, 67.34, 55.41, 54.94. HRMS (ESI) calcd for $C_{30}H_{27}NO_5$ $[M+H]^+$: 482.1917, Found: 482.1953.

(*E*)-4-(2-hydroxy-*N*-(4-methoxybenzyl)benzamido)but-2-en-1-yl methyl carbonate (1v)



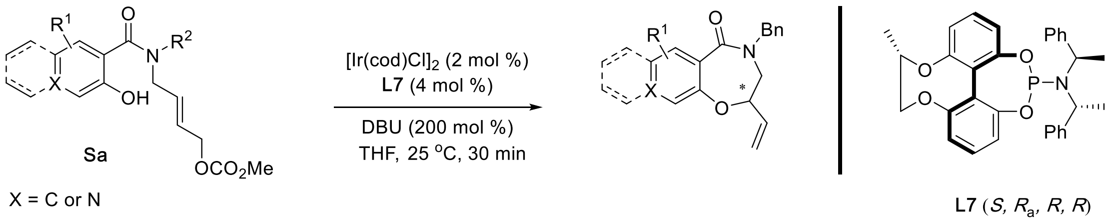
Yellow oil, 0.74 g, 96% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.03 (d, *J* = 8.2 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.81 (t, *J* = 7.4 Hz, 1H), 5.80 (m, 2H), 4.69 (s, 2H), 4.52 (d, *J* = 4.2 Hz, 2H), 4.12 (d, *J* = 5.3 Hz, 2H), 3.83 (s, 3H), 3.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.20, 171.15, 159.28, 158.78, 155.51, 132.74, 129.65, 128.81, 127.91, 127.62, 127.21, 118.73, 118.12, 114.36, 63.01, 60.40, 55.31, 54.87. HRMS (ESI) calcd for $C_{21}H_{23}NO_6$ $[M+H]^+$: 386.1598, Found: 386.1591.

(*Z*)-4-(2-hydroxy-*N*-(4-methoxybenzyl)benzamido)but-2-en-1-yl methyl carbonate ((*Z*)-1v)



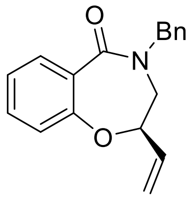
Yellow oil, 0.73 g, 95% yield; ^{1}H NMR (400 MHz,) δ 7.36 – 7.27 (m, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.03 (d, *J* = 8.2 Hz, 1H), 6.92 (d, *J* = 8.1 Hz, 2H), 6.81 (t, *J* = 7.5 Hz, 1H), 5.80 (m, 2H), 4.69 (s, 2H), 4.52 (d, *J* = 4.3 Hz, 2H), 4.14 – 4.10 (m, 2H), 3.83 (s, 3H), 3.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.20, 159.28, 158.78, 155.51, 132.74, 129.65, 128.81, 127.91, 127.62, 127.21, 118.73, 118.12, 117.57, 114.36, 67.32, 63.01, 60.40, 55.31, 54.87.

3.2 General Procedure for the Allylic Etherification of 1



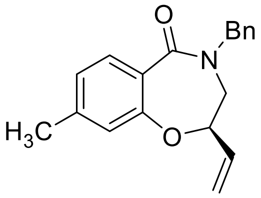
In a dry Schlenk tube filled with argon, $[Ir(cod)Cl]_2$ (2.7 mg, 0.004 mmol, 2 mol %), phosphoramidite ligand **L7** (4.1 mg, 0.008 mmol, 4 mol %), and *n*-propylamine (0.5 mL) were dissolved in THF (1.0 mL). The reaction mixture was heated at 50 °C for 30 min and then the volatile solvents were removed in vacuum to give a yellow solid. In this tube, allylic carbonates **1** (0.2 mmol), DBU (61 mg, 0.4 mmol, 200 mol %) and THF (2.0 mL) were added and stirred at 25 °C until the reaction was complete. Then the solvent was evaporated and the residue was purified by silica gel column chromatography using petroleum/EtOAc as the eluent to give the desired products. (**2v** is prepared from (***Z***)**-1v** in the same way.)

(*R*)-4-Benzyl-2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (2a)



R_f = 0.50 (petroleum/EtOAc = 2 : 1, v/v); yellow oil, 53.6 mg, 96% yield; 93% ee [Daicel Chiralcel IF-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 80/20, *v* = 1.0 mL•min^{-1}, T = 25 °C, λ = 254 nm, t_R (minor) = 12.051 min, t_R (major) = 12.358 min]; $[\alpha]_D^{25}$ = +4.3° (c = 0.70, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.47 – 7.42 (m, 1H), 7.40 – 7.35 (m, 4H), 7.35 – 7.29 (m, 1H), 7.23 (td, *J* = 7.6, 1.1 Hz, 1H), 7.03 (dd, *J* = 8.1, 0.8 Hz, 1H), 5.83 (ddd, *J* = 17.1, 10.6, 6.3 Hz, 1H), 5.35 (m, 1H), 5.26 (m, 1H), 5.16 (d, *J* = 14.8 Hz, 1H), 4.77 – 4.69 (m, 1H), 4.58 (d, *J* = 14.8 Hz, 1H), 3.40 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.84, 152.78, 137.01, 134.19, 132.74, 130.76, 128.79, 128.24, 127.75, 124.11, 122.57, 118.24, 84.10, 51.01, 49.60. HRMS (ESI) calcd for $C_{18}H_{17}NO_2$ $[M+H]^+$: 280.1341, Found: 280.1328.

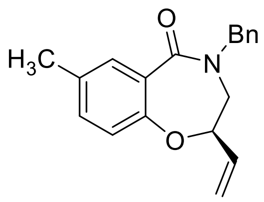
(*R*)-4-Benzyl-8-methyl-2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (2b)



R_f = 0.50 (petroleum/EtOAc = 2 : 1, v/v); yellow oil, 55.1 mg, 94% yield; 92% ee [Daicel Chiralcel IF-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 80/20, *v* = 1.0 mL•min^{-1}, T = 25 °C, λ = 254 nm, t_R (minor) = 13.913 min, t_R (major) =

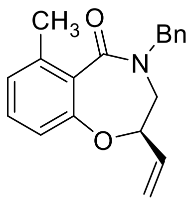
15.770 min]; $[\alpha]_D^{25}$ = +62.6° (c = 0.70, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.9 Hz, 1H), 7.43 – 7.31 (m, 5H), 7.09 – 7.00 (m, 1H), 6.88 – 6.78 (m, 1H), 5.82 (ddd, *J* = 17.0, 10.6, 6.3 Hz, 1H), 5.33 (m, 1H), 5.25 (m, 1H), 5.14 (d, *J* = 14.8 Hz, 1H), 4.71 (m, 1H), 4.57 (d, *J* = 14.8 Hz, 1H), 3.39 (m, 2H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.91, 152.78, 143.58, 137.11, 134.34, 130.72, 128.76, 128.24, 127.69, 125.05, 124.88, 122.84, 118.09, 83.93, 51.01, 49.75, 25.37, 21.34. HRMS (ESI) calcd for $C_{19}H_{19}NO_2$ $[M+H]^+$: 294.1498, Found: 294.1484.

(*R*)-4-Benzyl-7-methyl-2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (2c)



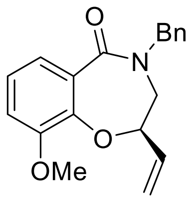
R_f = 0.50 (petroleum/EtOAc = 2 : 1, v/v); yellow oil, 58.1 mg, 99% yield; 96% ee [Daicel Chiralcel IA-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 93/7, *v* = 1.0 mL•min^{-1}, T = 25 °C, λ = 254 nm, t_R (minor) = 19.212 min, t_R (major) = 18.091 min]; $[\alpha]_D^{25}$ = +63.7° (c = 0.70, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.49 – 7.31 (m, 5H), 7.24 (d, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 5.83 (ddd, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.34 (d, *J* = 17.2 Hz, 1H), 5.25 (d, *J* = 10.6 Hz, 1H), 5.13 (d, *J* = 14.8 Hz, 1H), 4.76 – 4.66 (m, 1H), 4.59 (d, *J* = 14.8 Hz, 1H), 3.37 (m, 2H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.09, 150.50, 137.11, 134.33, 133.81, 133.38, 130.81, 128.77, 128.21, 128.05, 127.70, 122.37, 118.13, 83.90, 50.96, 49.63, 20.62. HRMS (ESI) calcd for $C_{19}H_{19}NO_2$ $[M+H]^+$: 294.1498, Found: 294.1483.

(*R*)-4-Benzyl-6-methyl-2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (2d)



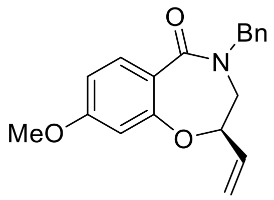
R_f = 0.50 (petroleum/EtOAc = 2 : 1, v/v); yellow oil, 55.1 mg, 94% yield; 99% ee [Daicel Chiralcel IA-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 90/10, *v* = 1.0 mL•min^{-1}, T = 25 °C, λ = 254 nm, t_R (minor) = 13.197 min, t_R (major) = 11.893 min]; $[\alpha]_D^{25}$ = +47.7° (c = 0.70, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (m, 6H), 7.09 (dd, *J* = 7.3, 2.9 Hz, 1H), 6.87 (dd, *J* = 7.7, 2.9 Hz, 1H), 5.93 – 5.73 (m, 1H), 5.30 (m, 2H), 5.13 (m, 1H), 4.72 – 4.58 (m, 2H), 3.39 – 3.24 (m, 2H), 2.55 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.13, 152.11, 139.56, 137.44, 134.26, 130.92, 128.77, 128.00, 127.66, 127.36, 120.40, 118.37, 83.38, 50.07, 48.95, 20.29. HRMS (ESI) calcd for $C_{19}H_{19}NO_2$ $[M+H]^+$: 294.1498, Found: 294.1483.

(*R*)-4-Benzyl-9-methoxy-2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (2e)



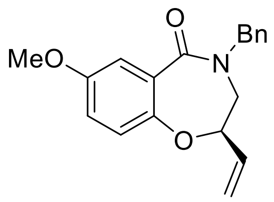
R_f = 0.40 (petroleum/EtOAc = 2 : 1, v/v); yellow oil, 59.4 mg, 96% yield; 99% ee [Daicel Chiralcel IA-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 90/10, *v* = 1.0 mL•min^{-1}, T = 25 °C, λ = 211 nm, t_R (minor) = 24.718 min, t_R (major) = 23.458 min]; $[\alpha]_D^{25}$ = +50.0° (c = 0.80, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (t, *J* = 10.3 Hz, 6H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 8.1 Hz, 1H), 5.85 (ddd, *J* = 17.1, 10.6, 6.6 Hz, 1H), 5.35 (d, *J* = 16.9 Hz, 1H), 5.21 (m, 2H), 4.86 – 4.72 (m, 1H), 4.56 (d, *J* = 14.7 Hz, 1H), 3.88 (s, 3H), 3.37 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.81, 152.39, 141.96, 137.09, 134.57, 130.23, 128.77, 128.19, 127.71, 124.47, 121.71, 118.00, 114.96, 84.72, 56.22, 50.92, 49.71. HRMS (ESI) calcd for $C_{19}H_{19}NO_3$ $[M+H]^+$: 310.1447, Found: 310.1432.

(*R*)-4-Benzyl-8-methoxy-2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (2f)



R_f = 0.40 (petroleum/EtOAc = 2 : 1, v/v); yellow oil, 60.0 mg, 97% yield; 91% ee [Daicel Chiralcel IA-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 85/15, *v* = 1.0 mL•min^{-1}, T = 25 °C, λ = 254 nm, t_R (minor) = 15.317 min, t_R (major) = 16.151 min]; $[\alpha]_D^{25}$ = +60.5° (c = 0.80, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.7 Hz, 1H), 7.42 – 7.31 (m, 5H), 6.76 (dd, *J* = 8.8, 2.2 Hz, 1H), 6.54 (d, *J* = 2.1 Hz, 1H), 5.83 (ddd, *J* = 17.0, 10.5, 6.3 Hz, 1H), 5.33 (d, *J* = 17.2 Hz, 1H), 5.25 (d, *J* = 10.5 Hz, 1H), 5.14 (d, *J* = 14.7 Hz, 1H), 4.72 (m, 1H), 4.55 (d, *J* = 14.8 Hz, 1H), 3.84 (s, 3H), 3.48 – 3.30 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.64, 163.33, 154.60, 137.16, 134.30, 132.40, 128.76, 128.27, 127.69, 119.92, 118.15, 110.21, 106.99, 84.00, 55.52, 51.14, 49.92. HRMS (ESI) calcd for $C_{19}H_{19}NO_3$ $[M+H]^+$: 310.1447, Found: 310.1432.

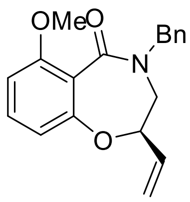
(*R*)-4-Benzyl-7-methoxy-2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (2g)



R_f = 0.50 (petroleum/EtOAc = 2 : 1, v/v); yellow oil, 59.4 mg, 96% yield; 94% ee [Daicel Chiralcel IA-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 90/10, *v* =

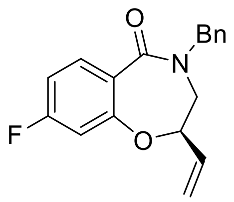
1.0 mL•min^{-1}, T = 25 °C, λ = 254 nm, t $_R$ (minor) = 20.603 min, t $_R$ (major) = 19.327 min]; $[\alpha]_D^{25}$ = +61.8° (c = 0.80, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.32 (m, 6H), 6.98 (m, 2H), 5.82 (ddd, *J* = 17.1, 10.6, 6.4 Hz, 1H), 5.33 (m, 1H), 5.25 (m, 1.1 Hz, 1H), 5.14 (d, *J* = 14.8 Hz, 1H), 4.68 (m, 1H), 4.59 (d, *J* = 14.8 Hz, 1H), 3.85 (s, 3H), 3.37 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.86, 156.15, 146.33, 137.06, 134.28, 129.16, 128.78, 128.20, 127.74, 123.69, 119.49, 118.21, 113.68, 83.92, 55.81, 51.03, 49.63. HRMS (ESI) calcd for $C_{19}H_{19}NO_3$ [M+H]$^+$: 310.1447, Found: 310.1432.

(*R*)-4-Benzyl-6-methoxy-2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (2h)



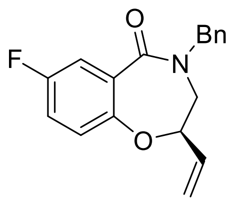
R_f = 0.40 (petroleum/EtOAc = 2 : 1, v/v); yellow oil, 53.8 mg, 87% yield; 96% ee [Daicel Chiralcel IA-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 75/25, *v* = 1.0 mL•min^{-1}, T = 25 °C, λ = 254 nm, t $_R$ (minor) = 17.409 min, t $_R$ (major) = 14.163 min]; $[\alpha]_D^{25}$ = +52.9° (c = 0.80, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (m, 6H), 6.82 (d, *J* = 8.4 Hz, 1H), 6.65 (d, *J* = 8.1 Hz, 1H), 5.85 – 5.72 (m, 1H), 5.25 (m, 3H), 4.56 (d, *J* = 14.9 Hz, 2H), 3.94 (s, 3H), 3.42 (m, 1H), 3.28 (m, 1H). ^{13}C NMR (101 MHz,) δ 166.01, 158.76, 152.92, 137.38, 134.21, 131.83, 128.73, 128.31, 127.66, 124.46, 123.97, 119.11, 118.53, 118.36, 115.34, 108.26, 83.56, 56.33, 49.91, 48.90. HRMS (ESI) calcd for $C_{19}H_{19}NO_3$ [M+H]$^+$: 310.1447, Found: 310.1433.

(*R*)-4-Benzyl-8-fluoro-2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (2i)



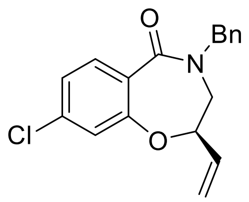
R_f = 0.60 (petroleum/EtOAc = 2 : 1, v/v); yellow oil, 58.8 mg, 99% yield; 91% ee [Daicel Chiralcel IA-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 85/15, *v* = 1.0 mL•min^{-1}, T = 25 °C, λ = 254 nm, t_R (minor) = 9.738 min, t_R (major) = 9.109 min]; $[\alpha]_D^{25}$ = +63.1° (c = 0.70, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (t, *J* = 7.6 Hz, 1H), 7.46 – 7.31 (m, 5H), 6.93 (t, *J* = 8.2 Hz, 1H), 6.75 (d, *J* = 9.5 Hz, 1H), 5.81 (ddd, *J* = 17.0, 10.4, 6.3 Hz, 1H), 5.30 (m, 2H), 5.15 (d, *J* = 14.8 Hz, 1H), 4.73 (s, 1H), 4.55 (d, *J* = 14.8 Hz, 1H), 3.53 – 3.32 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.87, 165.22 (d, *J* = 251.0 Hz), 154.57 (d, *J* = 12.0 Hz), 136.84, 133.81, 132.88 (d, *J* = 10.4 Hz), 128.83, 128.29, 127.84, 123.88 (d, *J* = 3.2 Hz), 118.48, 111.45, 111.23, 109.67, 109.44, 84.29, 51.19, 49.66. ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.79. HRMS (ESI) calcd for $C_{18}H_{16}FNO_2$ $[M+H]^+$: 298.1246, Found: 298.1234.

(*R*)-4-Benzyl-7-fluoro-2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (2j)



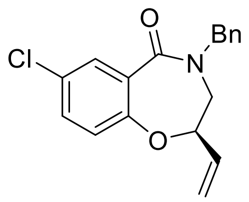
R_f = 0.60 (petroleum/EtOAc = 2 : 1, v/v); yellow oil, 55.3 mg, 93% yield; 91% ee [Daicel Chiralcel IA-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 95/5, *v* = 1.0 mL•min^{-1}, T = 25 °C, λ = 254 nm, t_R (minor) = 19.535 min, t_R (major) = 18.155 min]; $[\alpha]_D^{25}$ = +62.3° (c = 0.70, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 8.5, 3.1 Hz, 1H), 7.43 – 7.30 (m, 5H), 7.13 (td, *J* = 8.3, 3.0 Hz, 1H), 7.00 (dd, *J* = 8.8, 4.6 Hz, 1H), 5.81 (ddd, *J* = 17.0, 10.5, 6.3 Hz, 1H), 5.31 (m, 2H), 5.14 (d, *J* = 14.8 Hz, 1H), 4.70 (m, 1H), 4.56 (d, *J* = 14.8 Hz, 1H), 3.50 – 3.28 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.69, 159.03 (d, *J* = 242.0 Hz), 148.71 (d, *J* = 2.5 Hz), 136.77, 133.89, 129.77 (d, *J* = 7.4 Hz), 128.84, 128.25, 127.86, 124.05 (d, *J* = 8.0 Hz), 119.59, 119.36, 118.49, 117.02, 116.77, 84.05, 51.10, 49.47. ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.43. HRMS (ESI) calcd for $C_{18}H_{16}FNO_2$ $[M+H]^+$: 298.1246, Found: 298.1233.

(*R*)-4-Benzyl-8-chloro-2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (2k)



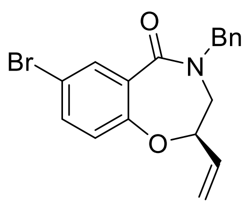
R_f = 0.60 (petroleum/EtOAc = 2 : 1, v/v); yellow oil, 60.1 mg, 96% yield; 90% ee [Daicel Chiralcel IA-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 85/15, *v* = 1.0 mL•min^{-1}, T = 25 °C, λ = 254 nm, t_R (minor) = 11.135 min, t_R (major) = 10.491 min]; $[\alpha]_D^{25}$ = -74.2° (c = 0.80, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.4 Hz, 1H), 7.45 – 7.31 (m, 5H), 7.20 (d, *J* = 8.3 Hz, 1H), 7.05 (s, 1H), 5.80 (ddd, *J* = 17.0, 10.5, 6.3 Hz, 1H), 5.31 (m, 2H), 5.14 (d, *J* = 14.7 Hz, 1H), 4.73 (m, 1H), 4.55 (d, *J* = 14.8 Hz, 1H), 3.41 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 167.83, 153.58, 138.16, 136.74, 133.73, 132.11, 128.85, 128.31, 127.88, 126.26, 124.30, 122.67, 118.58, 84.32, 51.18, 49.58. HRMS (ESI) calcd for $C_{18}H_{16}ClNO_2$ $[M+H]^+$: 314.0951, Found: 314.0936.

(*R*)-4-Benzyl-7-chloro-2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (2l)



R_f = 0.60 (petroleum/EtOAc = 2 : 1, v/v); yellow oil, 60.7 mg, 97% yield; 92% ee [Daicel Chiralcel IA-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 93/7, *v* = 1.0 mL•min^{-1}, T = 25 °C, λ = 254 nm, t $_R$ (minor) = 15.568 min, t $_R$ (major) = 14.780 min]; $[\alpha]_D^{25}$ = -76.9° (c = 0.80, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.36 (s, 6H), 6.97 (d, *J* = 8.4 Hz, 1H), 5.90 – 5.71 (m, 1H), 5.31 (m, 2H), 5.13 (d, *J* = 14.4 Hz, 1H), 4.72 (d, *J* = 4.7 Hz, 1H), 4.57 (d, *J* = 14.5 Hz, 1H), 3.55 – 3.25 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.48, 151.37, 136.69, 133.79, 132.62, 130.55, 129.41, 128.86, 128.27, 127.89, 124.01, 118.55, 84.11, 51.15, 49.46. HRMS (ESI) calcd for $C_{18}H_{16}ClNO_2$ $[M+H]^+$: 314.0951, Found: 314.0936.

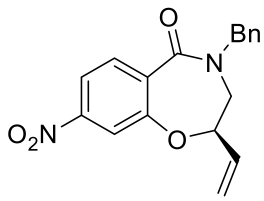
(*R*)-4-Benzyl-7-bromo-2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (2m)



R_f = 0.60 (petroleum/EtOAc = 2 : 1, v/v); brown oil, 60.7 mg, 85% yield; 91% ee [Daicel Chiralcel IA-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 95/5, *v* = 1.0 mL•min^{-1}, T = 25 °C, λ = 254 nm, t $_R$ (minor) = 20.457 min, t $_R$ (major) = 19.384 min]; $[\alpha]_D^{25}$ = -67.8° (c = 0.90, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 2.6 Hz, 1H), 7.53 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.41 – 7.32 (m, 5H), 6.91 (d, *J* = 8.6 Hz, 1H), 5.79 (ddd, *J* = 17.0, 10.6, 6.3 Hz, 1H), 5.30 (m, 2H), 5.12 (d, *J* = 14.7 Hz, 1H), 4.72 (m, 1H), 4.57 (d, *J* = 14.8 Hz, 1H), 3.47 – 3.29 (m, 2H).

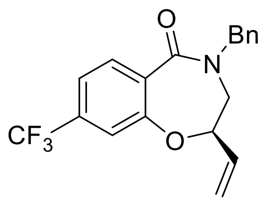
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.33, 151.92, 136.68, 135.57, 133.78, 133.53, 129.71, 128.86, 128.27, 127.89, 124.35, 118.54, 116.75, 84.09, 51.17, 49.46. HRMS (ESI) calcd for $C_{18}H_{16}BrNO_2$ $[M+H]^+$: 358.0446, Found: 358.0432.

(*R*)-4-Benzyl-8-nitro-2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (2n)



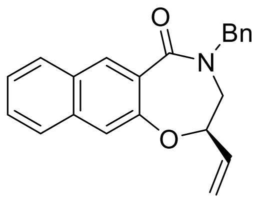
R_f = 0.40 (petroleum/EtOAc = 2 : 1, v/v); yellow oil, 58.3 mg, 90% yield; 84% ee [Daicel Chiralcel IF-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 85/15, *v* = 1.0 mL•min^{-1}, T = 25 °C, λ = 254 nm, t_R (minor) = 22.654 min, t_R (major) = 19.424 min]; $[\alpha]_D^{25}$ = +21.3° (c = 0.50, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 2H), 7.88 (s, 1H), 7.50 – 7.30 (m, 6H), 5.81 (ddd, *J* = 16.9, 10.5, 6.2 Hz, 1H), 5.40 – 5.31 (m, 2H), 5.17 (d, *J* = 14.7 Hz, 1H), 4.80 (m, 1H), 4.57 (d, *J* = 14.7 Hz, 1H), 3.48 – 3.40 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.68, 153.38, 150.48, 136.27, 133.54, 133.14, 132.27, 128.97, 128.37, 128.11, 119.12, 118.47, 117.99, 84.67, 51.32, 49.28. HRMS (ESI) calcd for $C_{18}H_{16}N_2O_4$ $[M+H]^+$: 325.1192, Found: 325.1180.

(*R*)-4-Benzyl-8-(trifluoromethyl)-2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (2o)



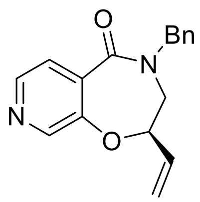
R_f = 0.40 (petroleum/EtOAc = 2 : 1, v/v); pale yellow oil, 57.6 mg, 83% yield; 80% ee [Daicel Chiralcel IA-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 90/10, *v* = 1.0 mL•min^{-1}, T = 25 °C, λ = 254 nm, t_R (minor) = 12.495 min, t_R (major) = 11.473 min]; $[\alpha]_D^{25}$ = -49.1° (c = 0.60, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.7 Hz, 1H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.43 – 7.28 (m, 6H), 5.91 – 5.74 (m, 1H), 5.33 (m, 2H), 5.17 (d, *J* = 14.8 Hz, 1H), 4.84 – 4.71 (m, 1H), 4.57 (d, *J* = 14.6 Hz, 1H), 3.51 – 3.32 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.43, 153.05, 136.54, 133.54, 131.88, 131.02, 128.90, 128.32, 127.98, 120.50 (d, *J* = 3.6 Hz), 119.77 (d, *J* = 3.7 Hz), 118.77, 84.46, 51.22, 49.42. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.08. HRMS (ESI) calcd for $C_{19}H_{16}F_3NO_2$ $[M+H]^+$: 348.1216, Found: 348.1200.

(*R*)-4-Benzyl-2-vinyl-3,4-dihydronaphtho[2,3-*f*][1,4]oxazepin-5(2*H*)-one (2p)



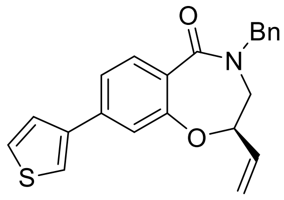
R_f = 0.60 (petroleum/EtOAc = 2 : 1, v/v); pale yellow oil, 61.2 mg, 93% yield; 91% ee [Daicel Chiralcel IF-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 85/15, *v* = 1.0 mL•min^{-1}, T = 25 °C, λ = 254 nm, t_R (minor) = 32.663 min, t_R (major) = 34.811 min]; $[\alpha]_D^{25}$ = -19.6° (c = 0.50, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.52 – 7.44 (m, 2H), 7.38 (dd, *J* = 16.3, 7.7 Hz, 5H), 5.91 (ddd, *J* = 17.2, 10.5, 6.6 Hz, 1H), 5.40 (d, *J* = 17.3 Hz, 1H), 5.31 (d, *J* = 10.6 Hz, 1H), 5.20 (d, *J* = 14.8 Hz, 1H), 4.74 (m, 1H), 4.65 (d, *J* = 14.8 Hz, 1H), 3.50 – 3.33 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.88, 149.30, 137.11, 135.66, 134.15, 131.45, 130.41, 129.49, 128.82, 128.23, 127.82, 126.92, 125.63, 119.46, 118.50, 83.42, 50.99, 49.42. HRMS (ESI) calcd for $C_{22}H_{19}NO_2$ $[M+H]^+$: 330.1502, Found: 330.1482.

(*R*)-4-Benzyl-2-vinyl-3,4-dihydropyrido[4,3-*f*][1,4]oxazepin-5(2*H*)-one (2q)



R_f = 0.30 (petroleum/EtOAc = 2 : 1, v/v); brown oil, 53.2 mg, 95% yield; 81% ee [Daicel Chiralcel IA-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 90/10, *v* = 1.0 mL•min^{-1}, T = 25 °C, λ = 254 nm, t $_R$ (minor) = 19.840 min, t $_R$ (major) = 18.608 min]; $[\alpha]_D^{25}$ = -15.0° (c = 0.50, CH_2Cl_2). ^1H NMR (400 MHz,) δ 8.47 (s, 2H), 7.83 (d, *J* = 2.7 Hz, 1H), 7.50 – 7.33 (m, 5H), 5.79 (m, 1H), 5.41 – 5.26 (m, 2H), 5.17 (d, *J* = 14.2 Hz, 1H), 4.80 (s, 1H), 4.54 (d, *J* = 14.5 Hz, 1H), 3.45 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.50, 148.49, 144.77, 144.44, 136.17, 133.29, 132.64, 128.95, 128.40, 128.09, 123.85, 118.75, 84.14, 51.47, 49.67. HRMS (ESI) calcd for $C_{17}H_{16}N_2O_2$ $[M+H]^+$: 281.1292, Found: 281.1280.

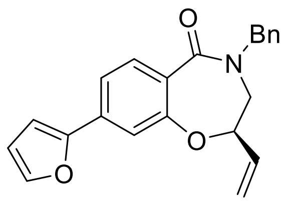
(*R*)-4-Benzyl-8-(thiophen-3-yl)-2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (2r)



R_f = 0.60 (petroleum/EtOAc = 2 : 1, v/v); pale yellow oil, 68.6 mg, 95% yield; 92% ee [Daicel Chiralcel IA-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 85/15, *v* = 1.0 mL•min^{-1}, T = 25 °C, λ = 254 nm, t $_R$ (minor) = 22.499 min, t $_R$ (major) = 26.072 min]; $[\alpha]_D^{25}$ = -5.7° (c = 0.60, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ

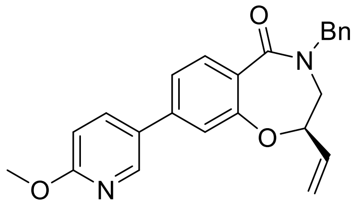
7.91 (d, *J* = 8.0 Hz, 1H), 7.56 (s, 1H), 7.51 – 7.27 (m, 9H), 5.86 (ddd, *J* = 17.0, 10.1, 6.7 Hz, 1H), 5.37 (d, *J* = 17.2 Hz, 1H), 5.28 (d, *J* = 10.5 Hz, 1H), 5.18 (d, *J* = 14.7 Hz, 1H), 4.76 (s, 1H), 3.46 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.57, 153.35, 140.84, 140.31, 137.02, 134.23, 131.54, 128.81, 128.30, 127.77, 126.62, 126.25, 126.14, 121.89, 121.69, 120.03, 118.32, 84.08, 51.14, 49.76. HRMS (ESI) calcd for $C_{22}H_{19}NO_2S$ $[M+H]^+$: 362.1223, Found: 362.1205.

(*R*)-4-Benzyl-8-(furan-2-yl)-2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (2s)



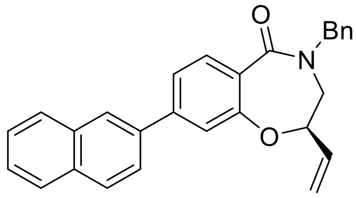
R_f = 0.60 (petroleum/EtOAc = 2 : 1, v/v); pale yellow oil, 67.0 mg, 97% yield; 92% ee [Daicel Chiralcel IA-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 85/15, *v* = 1.0 mL•min^{-1}, T = 25 °C, λ = 254 nm, t $_R$ (minor) = 14.863 min, t $_R$ (major) = 15.557 min]; $[\alpha]_D^{25}$ = -8.4° (c = 0.60, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.1 Hz, 1H), 7.52 (d, *J* = 6.5 Hz, 2H), 7.45 – 7.28 (m, 6H), 6.77 (s, 1H), 6.52 (s, 1H), 5.86 (ddd, *J* = 17.1, 10.5, 6.4 Hz, 1H), 5.36 (d, *J* = 17.2 Hz, 1H), 5.28 (d, *J* = 10.6 Hz, 1H), 5.16 (d, *J* = 14.8 Hz, 1H), 4.75 (s, 1H), 4.58 (d, *J* = 14.8 Hz, 1H), 3.55 – 3.33 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.50, 153.35, 152.60, 142.96, 137.01, 135.10, 134.20, 131.47, 128.80, 128.30, 127.77, 126.41, 119.23, 118.31, 117.35, 111.94, 106.99, 84.06, 51.11, 49.72. HRMS (ESI) calcd for $C_{22}H_{19}NO_3$ $[M+H]^+$: 346.1451, Found: 346.1433.

(*R*)-4-Benzyl-8-(6-methoxypyridin-3-yl)-2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (2t)



R_f = 0.60 (petroleum/EtOAc = 2 : 1, v/v); pale yellow oil, 74.1 mg, 96% yield; 92% ee [Daicel Chiralcel IA-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 85/15, v = 1.0 mL•min^{-1}, T = 25 °C, λ = 254 nm, t_R (minor) = 21.300 min, t_R (major) = 27.712 min]; $[\alpha]_D^{25}$ = -6.3° (c = 0.60, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 2.4 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.82 (dd, *J* = 8.6, 2.5 Hz, 1H), 7.42 – 7.31 (m, 6H), 7.20 (d, *J* = 1.5 Hz, 1H), 6.85 (d, *J* = 8.6 Hz, 1H), 5.85 (ddd, *J* = 17.0, 10.6, 6.3 Hz, 1H), 5.36 (d, *J* = 17.2 Hz, 1H), 5.27 (d, *J* = 10.6 Hz, 1H), 5.18 (d, *J* = 14.8 Hz, 1H), 4.77 (m, 1H), 4.58 (d, *J* = 14.8 Hz, 1H), 4.01 (s, 3H), 3.45 (m, 2H). ^{13}C NMR (101 MHz, CDCl3) δ 168.48, 164.07, 153.39, 145.09, 142.51, 137.39, 136.95, 134.10, 131.72, 128.83, 128.53, 128.28, 127.80, 126.51, 122.01, 120.28, 118.40, 111.05, 84.13, 53.74, 51.14, 49.71. HRMS (ESI) calcd for $C_{24}H_{22}N_2O_3$ $[M+H]^+$: 387.1719, Found: 387.1698.

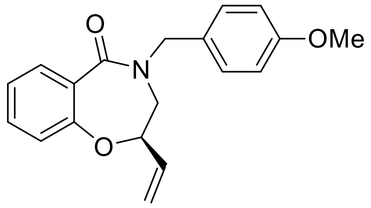
(*R*)-4-Benzyl-8-(naphthalen-2-yl)-2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (2u)



R_f = 0.60 (petroleum/EtOAc = 2 : 1, v/v); pale yellow oil, 76.2 mg, 94% yield; 94% ee [Daicel Chiralcel IF-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 90/10, v = 1.0 mL•min^{-1}, T = 25 °C, λ = 254 nm, t_R (minor) = 42.743 min, t_R (major) = 38.050 min]; $[\alpha]_D^{25}$ = +22.1° (c = 0.70, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.8 Hz, 1H), 7.93 (t, *J* = 9.5 Hz, 3H), 7.60 – 7.35 (m, 10H), 7.22

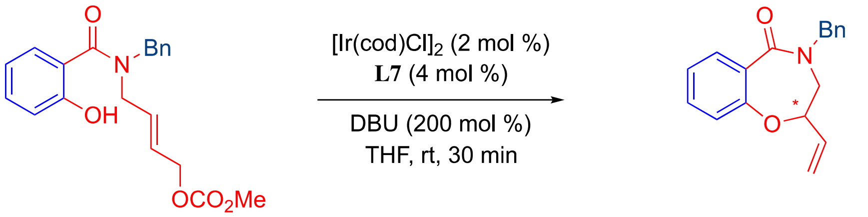
(s, 1H), 5.94 – 5.80 (m, 1H), 5.37 (d, *J* = 17.2 Hz, 1H), 5.25 (m, 2H), 4.80 (s, 1H), 4.64 (d, *J* = 14.8 Hz, 1H), 3.54 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.74, 152.77, 145.69, 138.71, 137.05, 134.20, 133.81, 131.20, 130.83, 128.84, 128.38, 128.29, 127.81, 126.83, 126.70, 126.34, 125.97, 125.86, 125.68, 125.32, 124.01, 118.27, 84.11, 51.17, 49.82. HRMS (ESI) calcd for $C_{24}H_{22}N_2O_3$ $[M+H]^+$: 406.1807, Found: 406.1794.

(*R*)-4-(4-Methoxybenzyl)-2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (2v)



Trans-substrate: R_f = 0.60 (petroleum/EtOAc= 2 : 1, v/v); pale yellow oil, 57.5 mg, 93% yield; 90% ee [Daicel Chiralcel IA-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 95/5, *v* = 1.0 mL•min^{-1}, t = 25 °C, λ = 254 nm, t_R (minor) = 35.879 min, t_R (major) = 33.676 min]; $[\alpha]_D^{25}$ = +4.5° (c = 0.50, CH_2Cl_2). **Cis-substrate:** R_f = 0.60 (petroleum/EtOAc= 2 : 1, v/v); pale yellow oil, 58.7 mg, 95% yield; -73% ee [Daicel Chiralcel IA-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 95/5, *v* = 1.0 mL•min^{-1}, t = 25 °C, λ = 254 nm, t_R (minor) = 34.931 min, t_R (major) = 36.551 min]; $[\alpha]_D^{25}$ = -4.1° (c = 0.50, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 8.1 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 2H), 5.82 (ddd, *J* = 17.0, 10.2, 6.6 Hz, 1H), 5.35 (d, *J* = 17.3 Hz, 1H), 5.26 (d, *J* = 10.6 Hz, 1H), 5.12 (d, *J* = 14.6 Hz, 1H), 4.70 (s, 1H), 4.49 (d, *J* = 14.6 Hz, 1H), 3.83 (s, 3H), 3.47 – 3.30 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.72, 159.25, 152.76, 134.28, 132.66, 130.76, 129.67, 129.12, 128.36, 124.06, 122.54, 118.15, 114.17, 55.31, 50.45, 49.40. HRMS (ESI) calcd for $C_{19}H_{19}NO_3$ $[M+H]^+$: 310.1393, Found: 310.1433.

3.3 Gram-scale Reaction



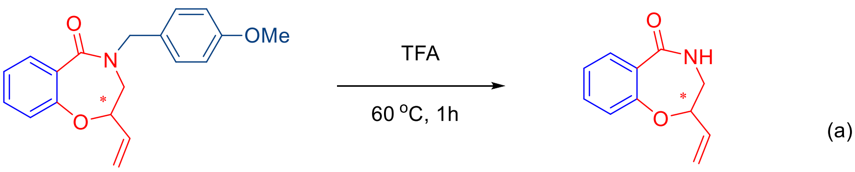
1a 1 g

2a 0.72 g

92% yield, 91% *ee*

Representative Procedure: in a dry Schlenk tube (50.0 mL) filled with argon, $[Ir(cod)Cl]_2$ (37.8 mg, 0.056 mmol, 2 mol %), ligand **L7** (57.6 mg, 0.113 mmol, 4 mol %), and *n*-propylamine (5.0 mL) were dissolved in THF (10.0 mL). The reaction mixture was heated at 50 °C for 30 min and then the volatile solvents were removed in vacuum to give a yellow solid. In glove box, substrate (1 g, 2.82 mmol), DBU (0.857g, 5.64 mmol, 200 mol %) and solvent (20.0 mL) were added into the above tube and stirred at 25 °C until the reaction was complete. Then the solvent was evaporated and the residue was purified by silica gel column chromatography using petroleum/EtOAc as the eluent to give the desired product (92% yield, 91% ee).

3.4 Procedure for the Synthesis of 3v

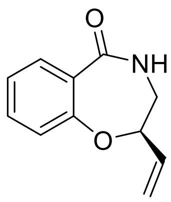


30.9 mg, 90% *ee*
2v

16.8 mg, 89% yield,89% *ee*
3v

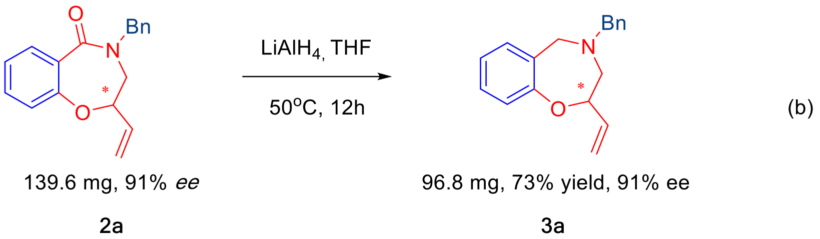
In a dry Schlenk tube filled with argon, **2v** (30.9 mg, 0.1 mmol) was dissolved in excessive TFA (10 mL). The reaction mixture was heated at 60 °C for 1 h. Then the crude reaction mixture was diluted with DCM (10 mL) and washed with saturated sodium bicarbonate solution (10 mL x 3) and brine (10 mL x 3). The combined organic layers were dried over Na_2SO_4. Afterwards, the solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography (petroleum/EtOAc = 1 : 1) to afford the desired products **3v** (89% yield, 89% ee).

(*R*)-2-Vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (3v)



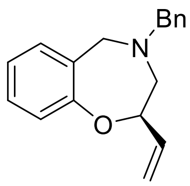
R_f = 0.10 (petroleum/EtOAc = 2 : 1, v/v); black oil, 16.8 mg, 89% yield; 89% ee [Daicel Chiralcel IF-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 95/5, *v* = 1.0 mL•min^{-1}, T = 25 °C, λ = 254 nm, t_R (minor) = 31.262 min, t_R (major) = 32.378 min]; $[\alpha]_D^{25}$ = +12.6° (c = 0.30, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.32 – 7.18 (m, 2H), 7.09 (d, *J* = 8.1 Hz, 1H), 6.05 – 5.89 (m, 1H), 5.48 (d, *J* = 17.1 Hz, 1H), 5.35 (d, *J* = 10.6 Hz, 1H), 4.94 (s, 1H), 3.50 (d, *J* = 14.5 Hz, 1H), 3.40 – 3.27 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.17, 154.03, 134.26, 133.29, 130.86, 126.11, 123.77, 122.55, 118.39, 84.44, 44.63. HRMS (ESI) calcd for $C_{11}H_{11}NO_2$ $[M+H]^+$: 190.0863, Found: 190.0859.

3.5 Procedure for the Synthesis of 3a



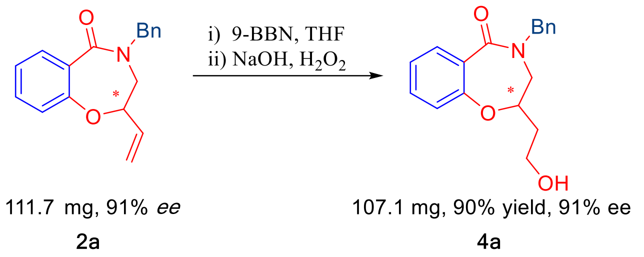
To a solution of **2a** (139.6 mg, 0.5 mmol) in THF (10 mL) at 0 °C, $LiAlH_4$ (114 mg, 3 mmol) was added in three portions. The reaction mixture was stirred for 12 h at 50 °C. It was cooled back down to 0 °C and MeOH was added. Then the mixture was filtered through celite and the obtained solution was concentrated in vacuo. The crude residue was purified using column chromatography (eluent: petroleum ether/EtOAc = 2 : 1) to provide the desired product **3a** (73% yield, 91% ee).

(*R*)-4-Benzyl-2-vinyl-2,3,4,5-tetrahydrobenzo[*f*][1,4]oxazepine (3a)



R_f = 0.30 (petroleum/EtOAc = 2 : 1, v/v); yellow oil, 96.8 mg, 73% yield; 91% ee [Daicel Chiralcel IF-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol = 99.5/0.5, *v* = 1.0 mL•min^{-1}, T = 25 °C, λ = 254 nm, t_R (minor) = 5.744 min, t_R (major) = 5.327 min]; $[\alpha]_D^{25}$ = -9.5° (c = 0.40, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.24 (m, 6H), 7.14 – 7.00 (m, 3H), 5.94 (ddd, *J* = 16.0, 10.7, 5.2 Hz, 1H), 5.46 (m, 1H), 5.27 (m, 1H), 4.52 (d, *J* = 3.6 Hz, 1H), 4.08 (d, *J* = 14.2 Hz, 1H), 3.70 (m, 3H), 3.09 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.76, 138.43, 136.37, 131.97, 130.59, 128.99, 128.66, 128.40, 127.27, 123.58, 121.26, 116.03, 78.92, 62.41, 58.24, 56.97. HRMS (ESI) calcd for $C_{18}H_{19}NO$ $[M+H]^+$: 266.1539, Found: 266.1535.

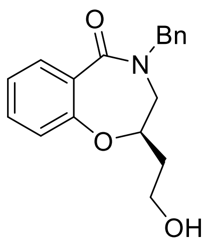
3.6 Procedure for the Synthesis of 4a



(c)

A flame dried Schlenk tube was cooled to room temperature and filled with argon. To this flask **2a** (111.7 mg, 0.4 mmol) and 9-BBN (0.5 M in THF, 2.4 mL, 1.2 mmol) were added. The reaction mixture was heated at 50 °C for 2 hours until the starting material was consumed completely (monitored by TLC). Then the reaction mixture was cooled to 0 °C, 3 M aqueous NaOH (0.8 mL) solution was added. After 5 min, 30% H_2O_2 (0.6 mL) was added by syringe. After stirring for an additional 3 hours at room temperature, saturated aqueous Na_2SO_3 solution was added, then the reaction mixture was extracted with EtOAc (10 mL x 3). The combined organic layers were washed with brine, separated, dried over Na_2SO_4 and concentrated by rotary evaporation. Then the residue was purified by silica gel column chromatography (PE/EA = 1/1) to afford the desired product **4a** (90% yield, 91% ee).

(*R*)-4-Benzyl-2-(2-hydroxyethyl)-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (4a)



R_f = 0.10 (petroleum/EtOAc = 2 : 1, v/v); white solid, 107.1 mg, 90% yield; 91% ee [Daicel Chiralcel IA-3 (0.46 cm x 25 cm), *n*-hexane/2-propanol =

80/20, v = 1.0 mL•min^{-1}, T = 25 °C, λ = 254 nm, t_R (minor) = 13.672 min, t_R (major) = 12.821 min]; $[\alpha]_D^{25}$ = +3.7° (c = 0.50, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 7.6 Hz, 1H), 7.49 – 7.31 (m, 6H), 7.22 (t, J = 7.4 Hz, 1H), 6.98 (d, J = 8.0 Hz, 1H), 5.01 (d, J = 14.8 Hz, 1H), 4.72 (d, J = 14.8 Hz, 1H), 4.50 (s, 1H), 3.85 (m, 2H), 3.40 – 3.28 (m, 2H), 1.91 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.94, 152.36, 137.07, 132.69, 130.84, 128.79, 128.45, 128.21, 127.74, 124.11, 122.55, 81.69, 59.41, 51.03, 50.03, 34.57. HRMS (ESI) calcd for $C_{18}H_{19}NO_3$ $[M+H]^+$: 298.1438, Found: 298.1433.

4.Copies of NMR Spectra

Figure 1. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1a

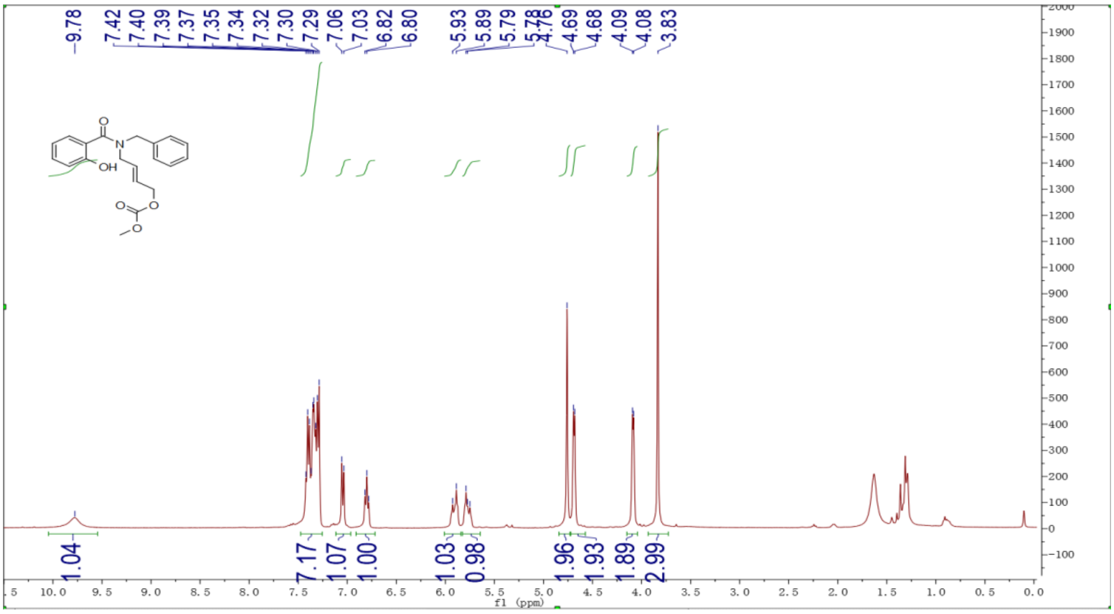


Figure 2. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 1a

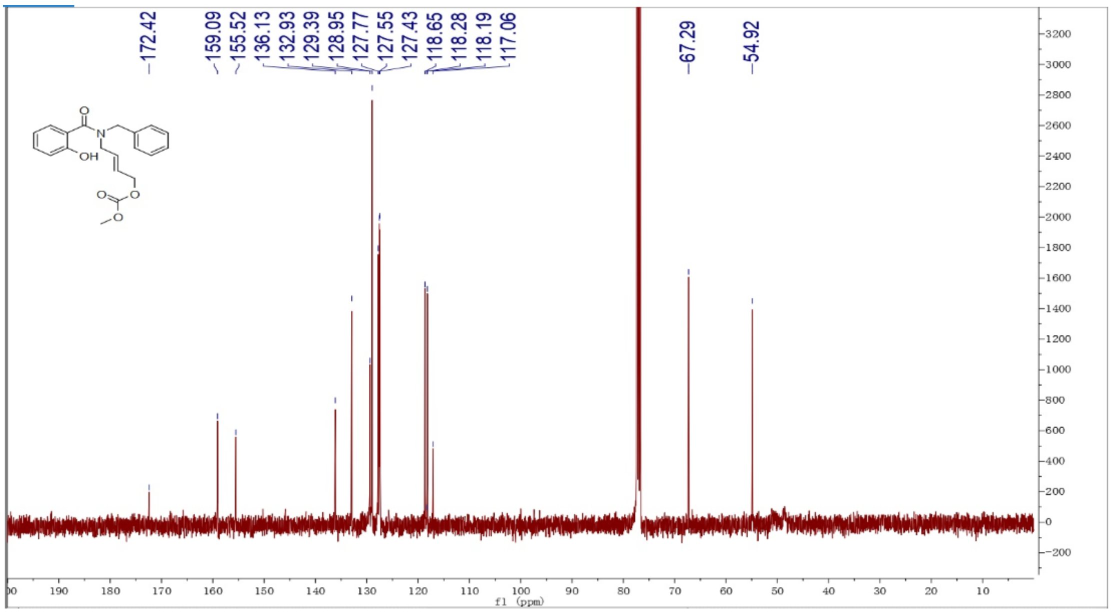


Figure 3. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1b

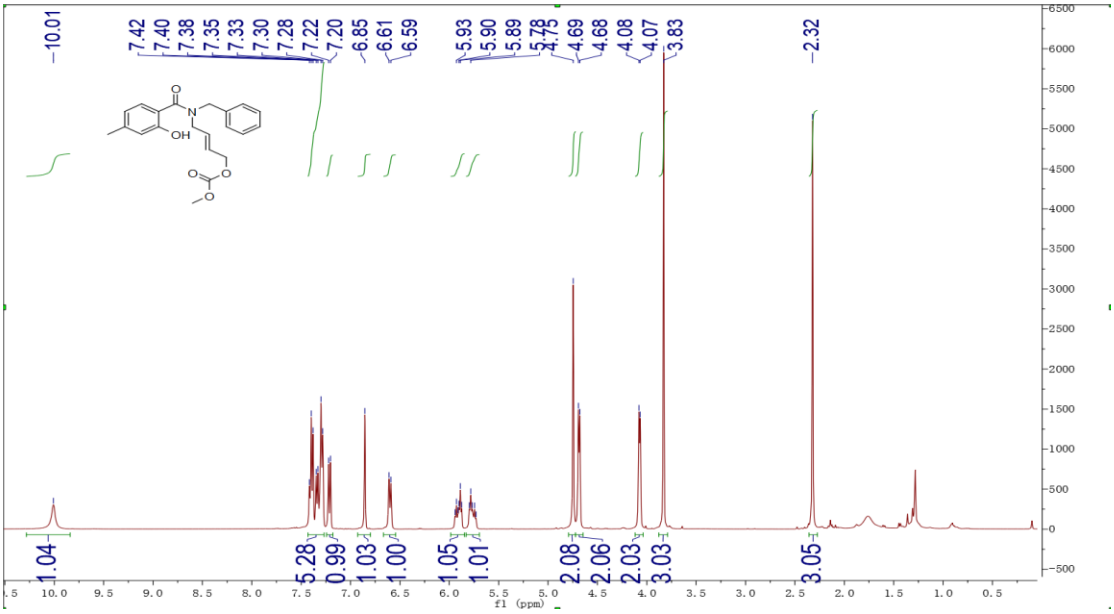


Figure 4. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 1b

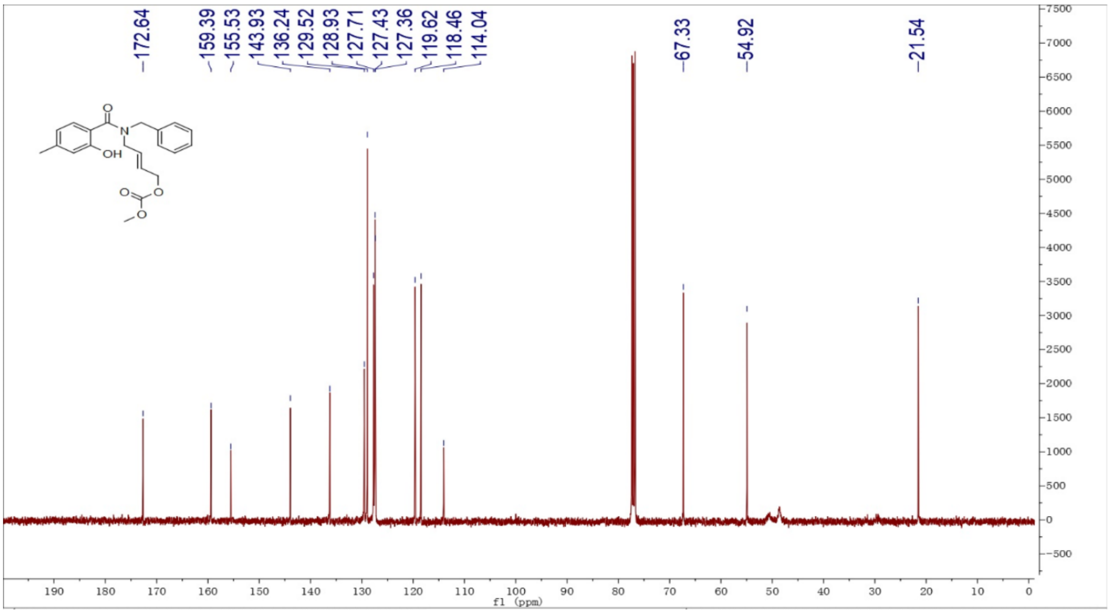


Figure 5. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1c

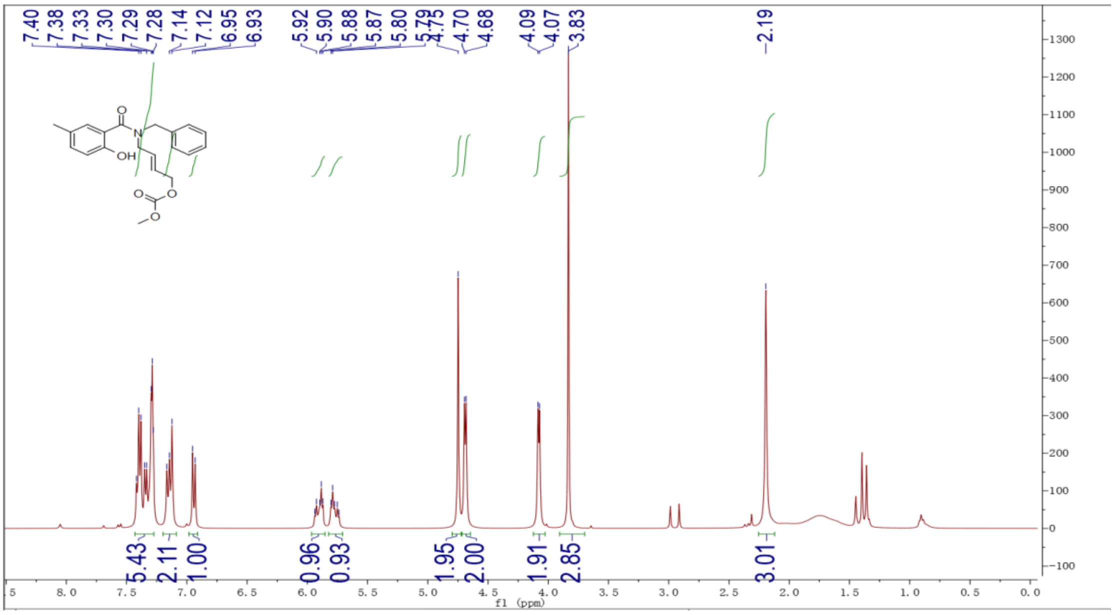


Figure 6. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 1c

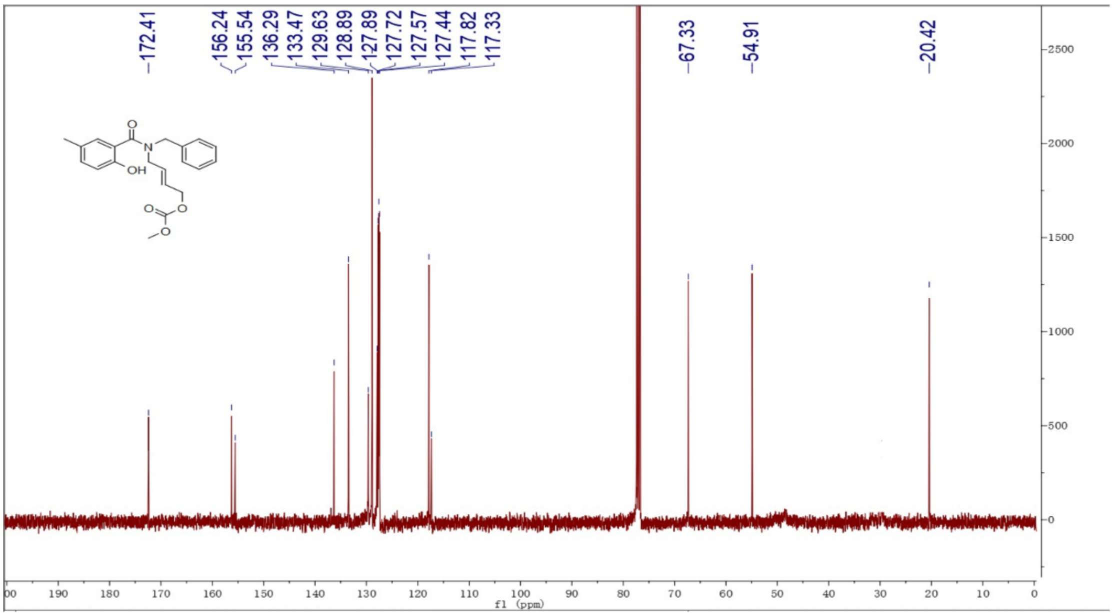


Figure 7. [1]H NMR (400 MHz, CDCl$_3$) spectrum of 1d

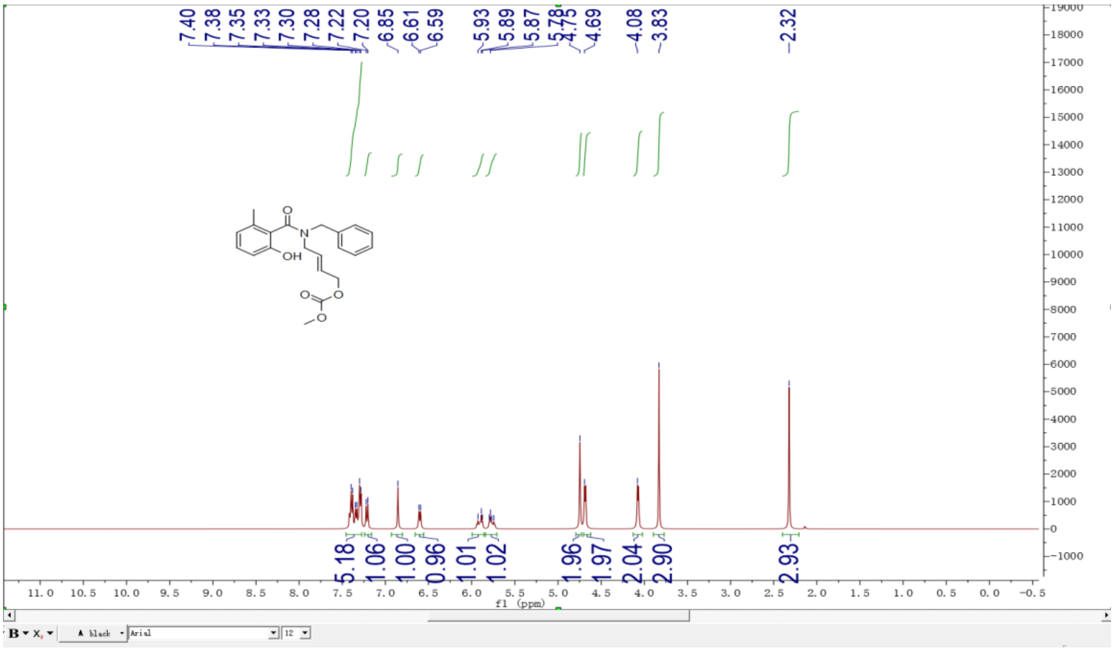


Figure 8. [13]C NMR (100 MHz, CDCl$_3$) spectrum of 1d

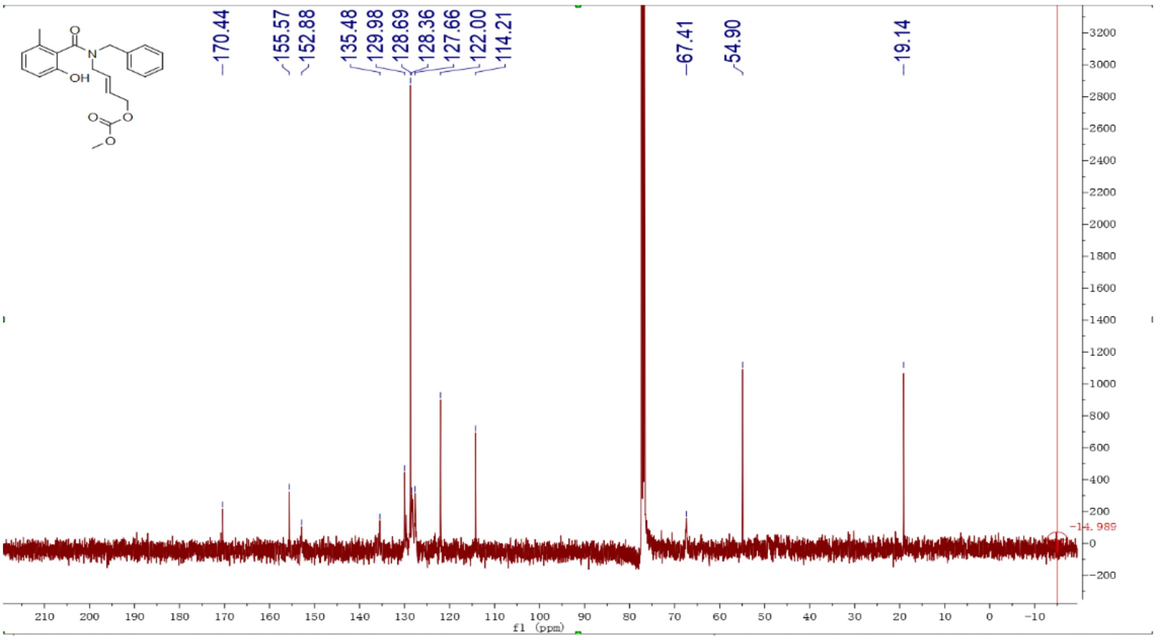


Figure 9. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1e

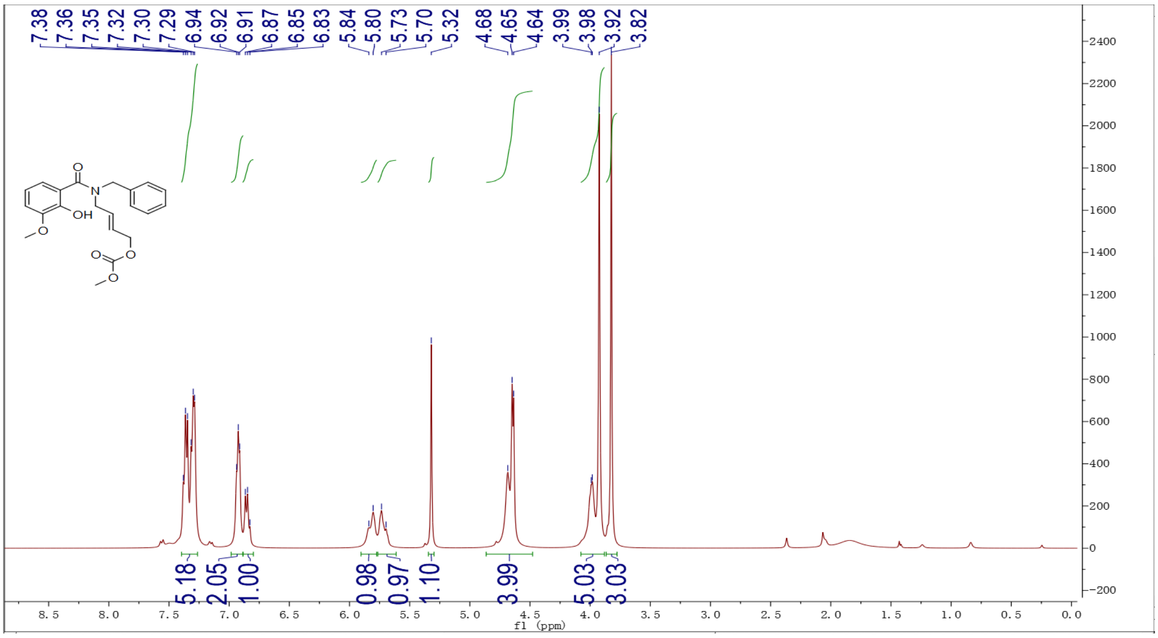


Figure 10. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 1e

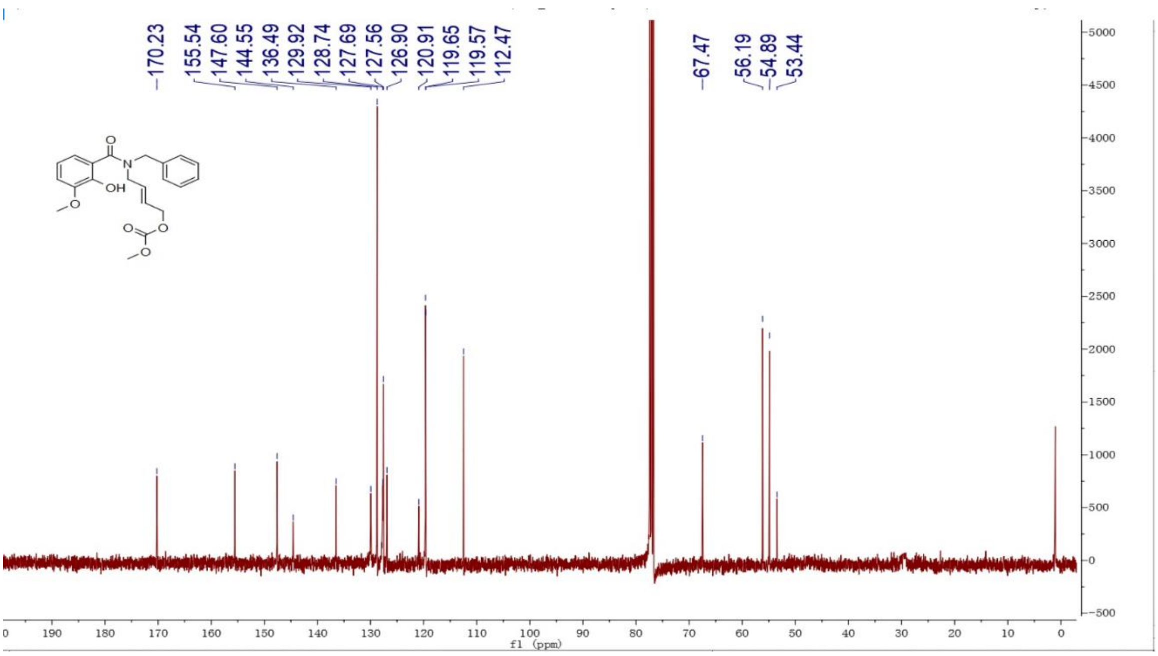


Figure 11. ^{1}H **NMR (400 MHz, $CDCl_3$) spectrum of 1f**

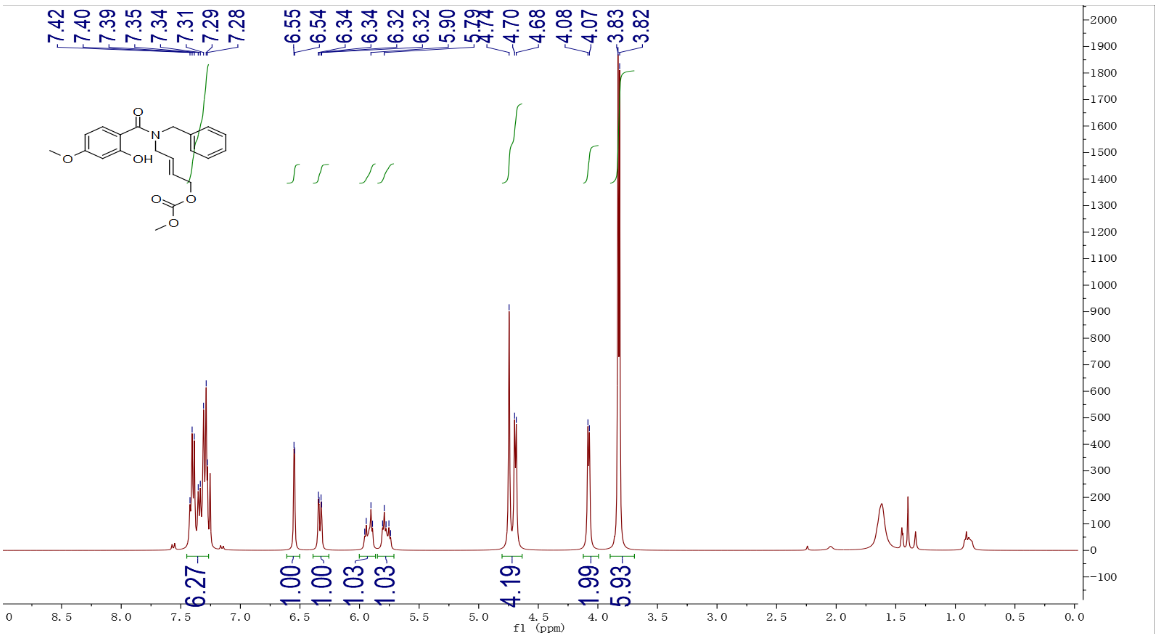


Figure 12. ^{13}C **NMR (100 MHz, $CDCl_3$) spectrum of 1f**

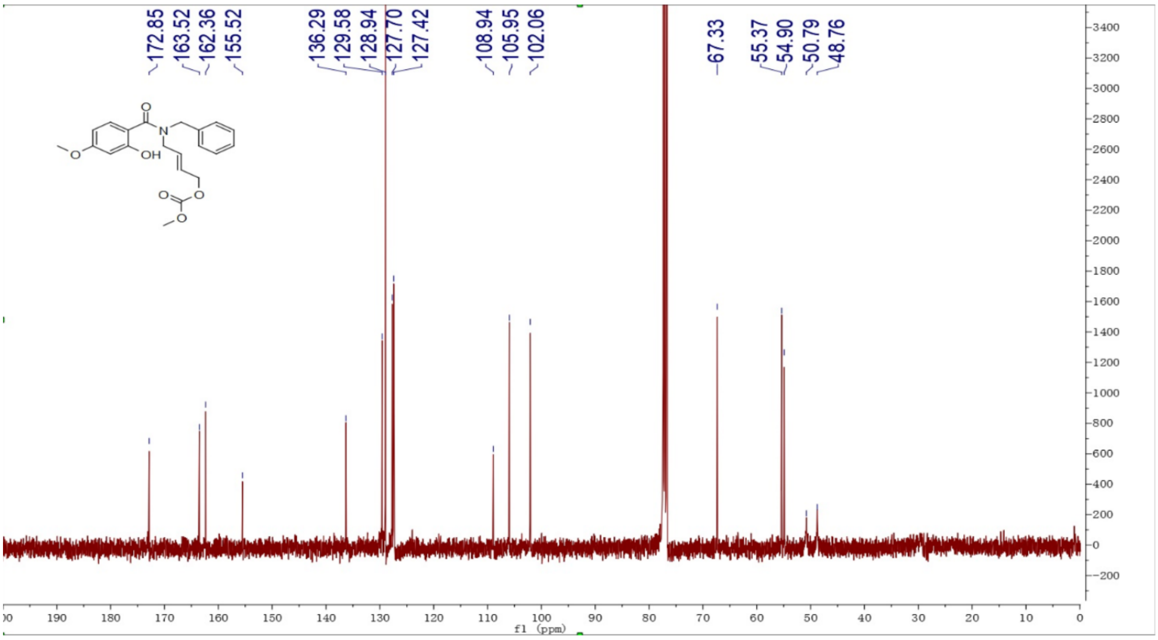


Figure 13. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of 1g

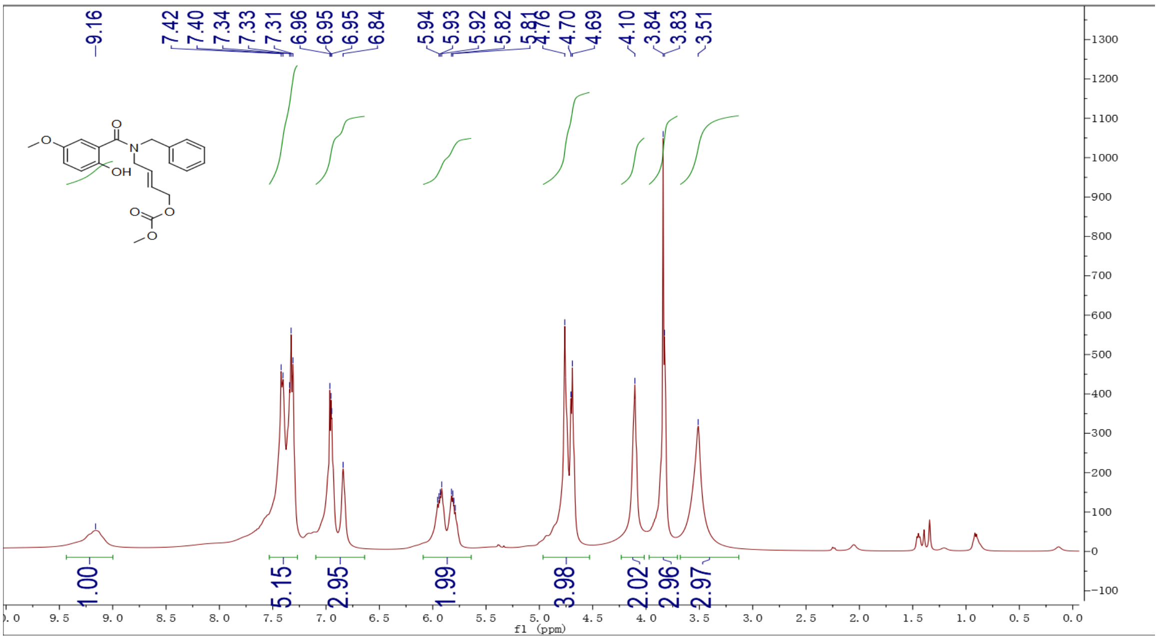


Figure 14. ^{13}C NMR (100 MHz, CDCl$_3$) spectrum of 1g

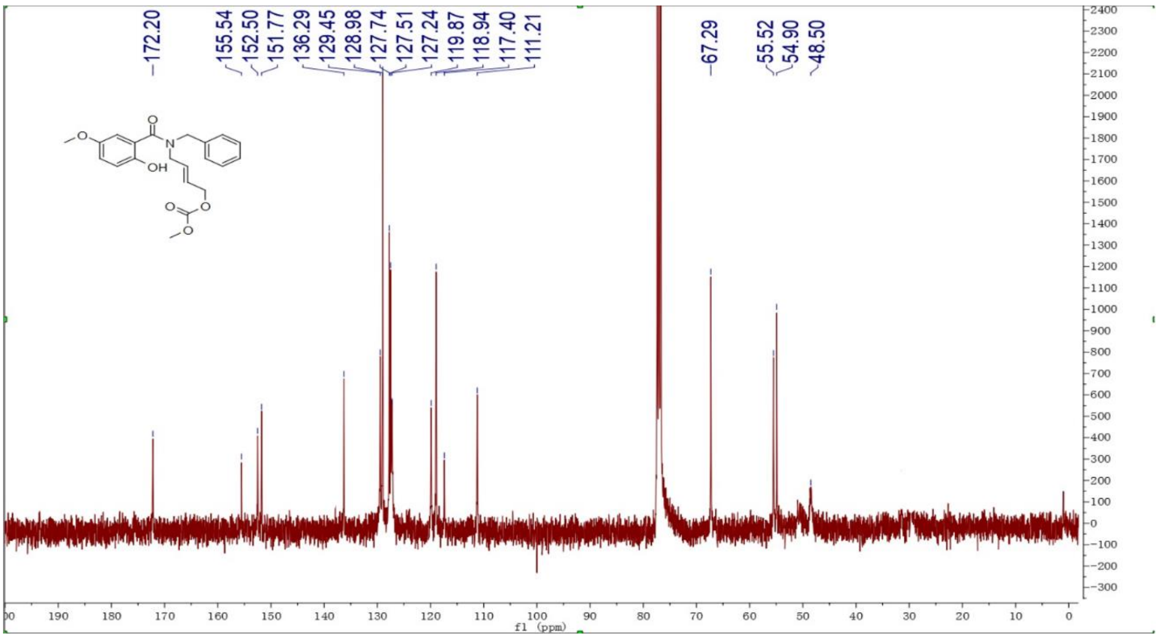


Figure 15. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1h

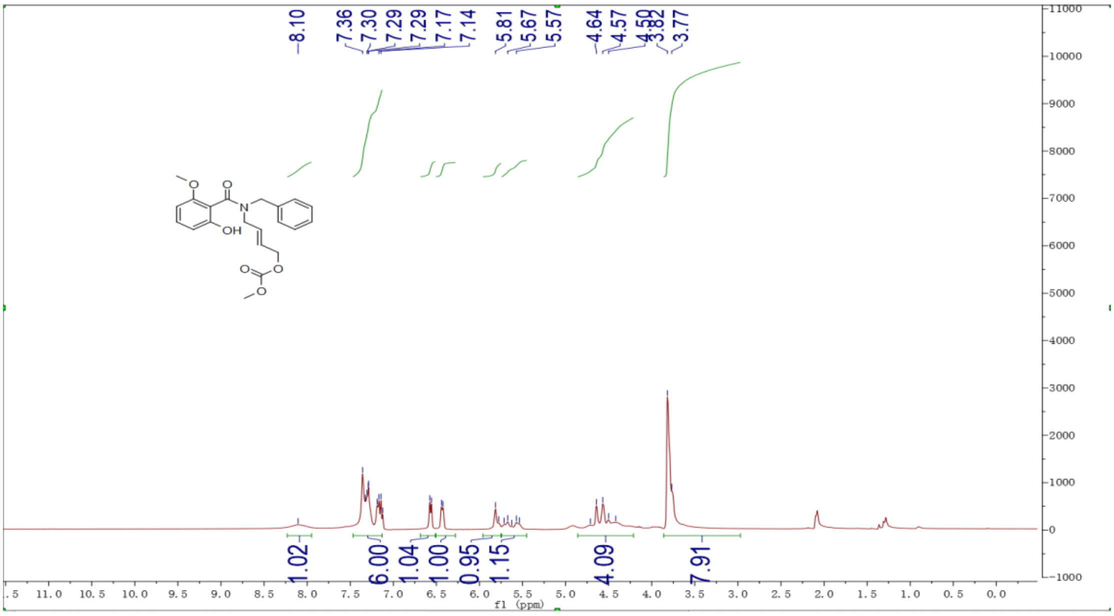


Figure 16. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 1h

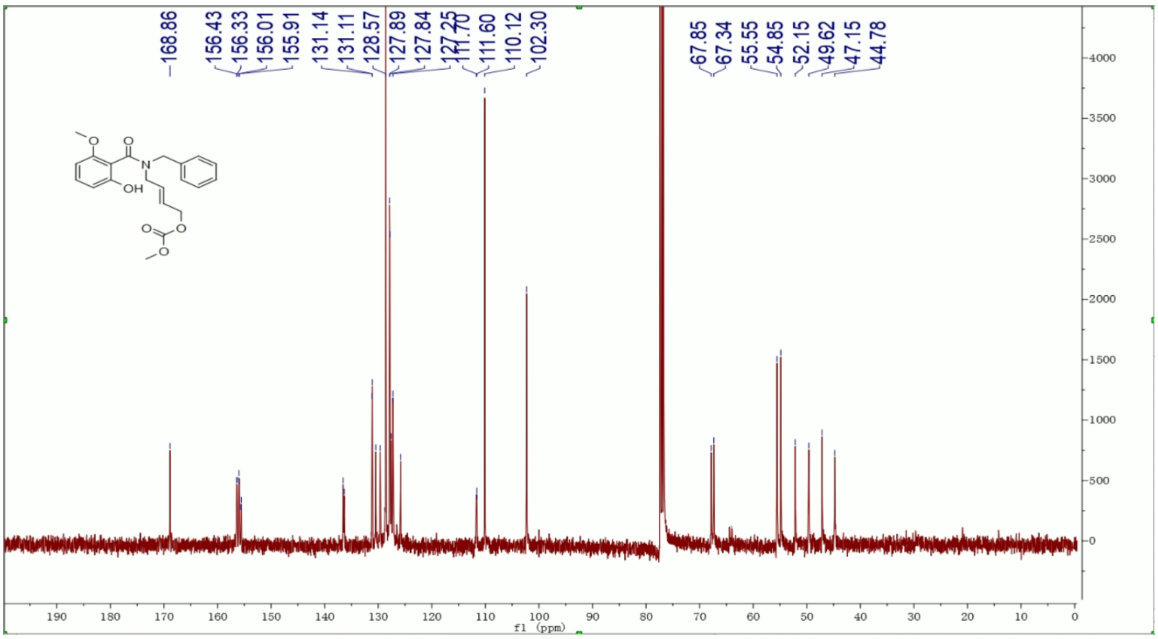


Figure 17. ^{1}H **NMR (400 MHz,** $CDCl_3$**) spectrum of 1i**

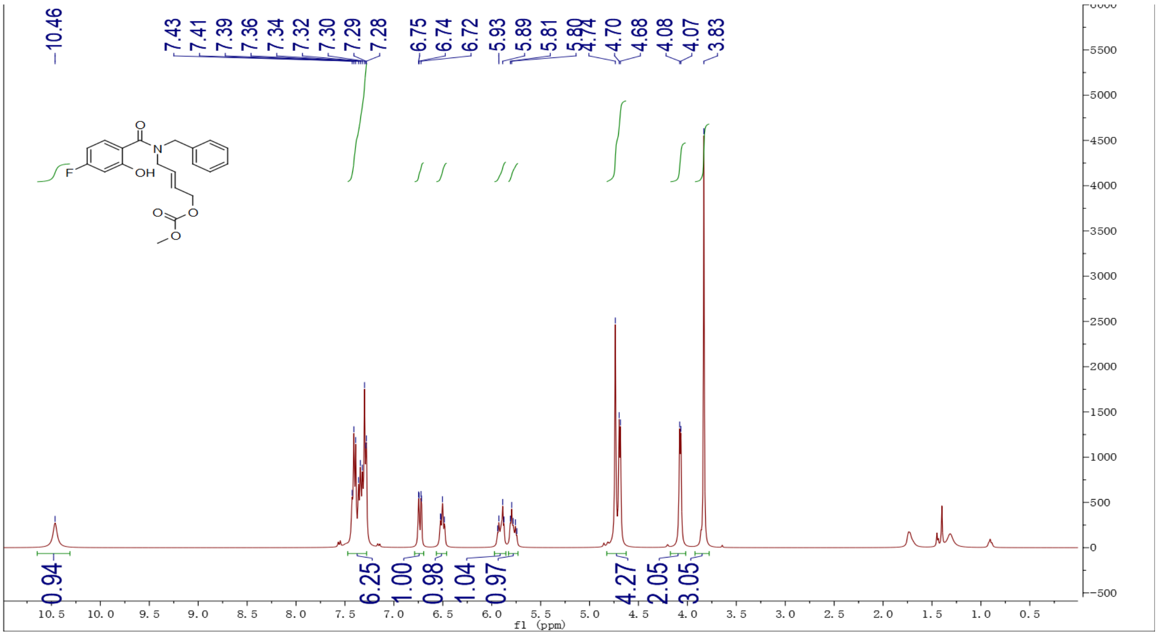


Figure 18. ^{13}C **NMR (100 MHz,** $CDCl_3$**) spectrum of 1i**

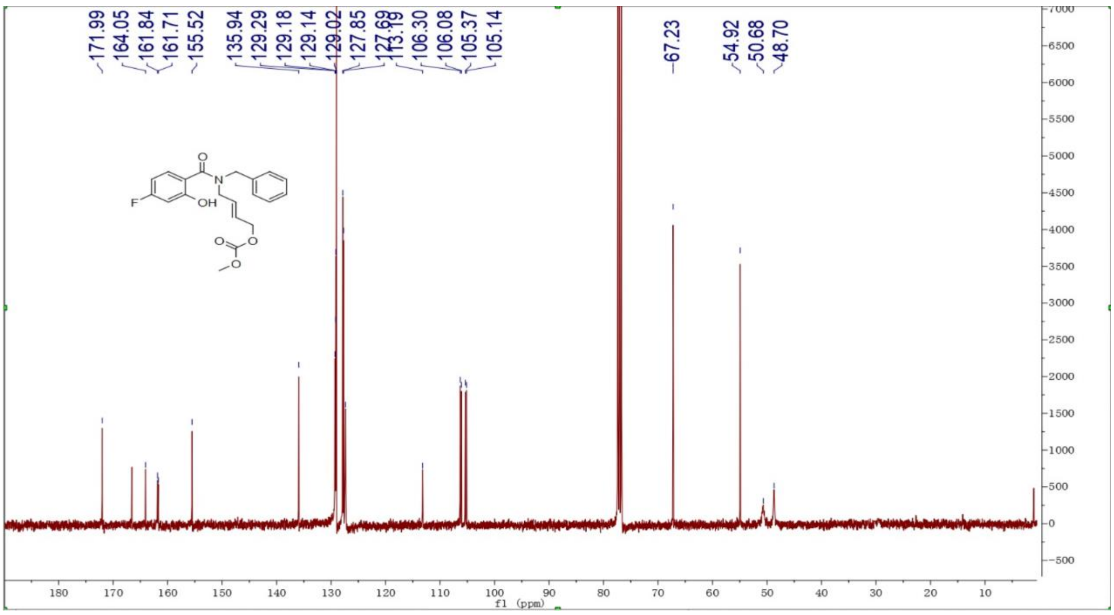


Figure 19. ^{19}**F NMR (376 MHz, CDCl$_3$) spectrum of 1i**

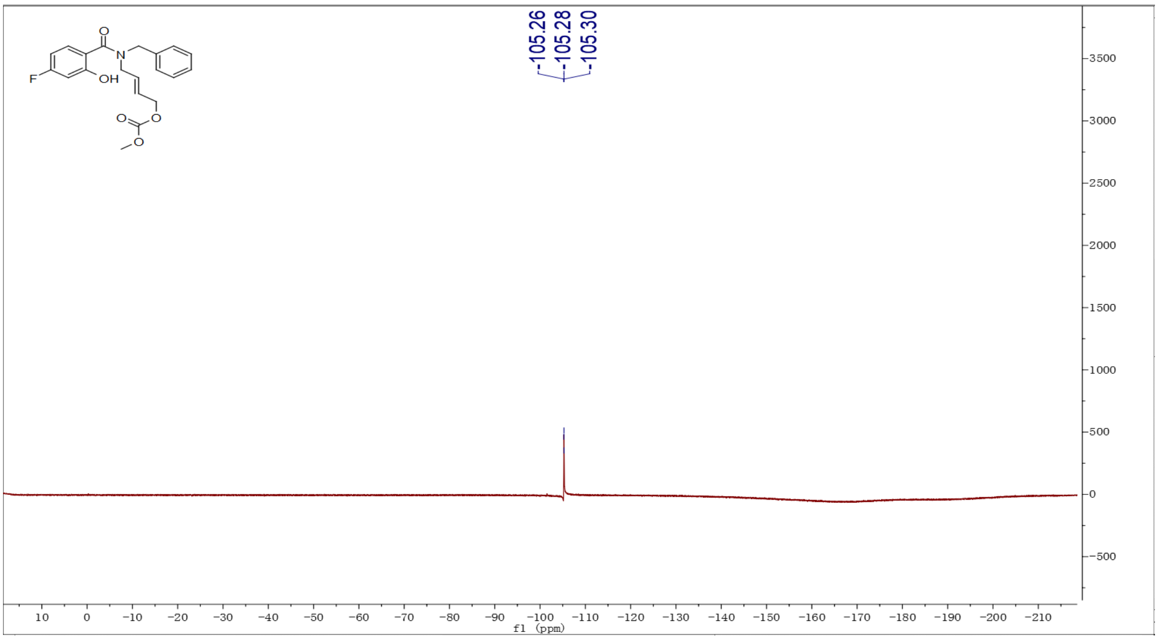


Figure 20. ^{1}**H NMR (400 MHz, CDCl$_3$) spectrum of 1j**

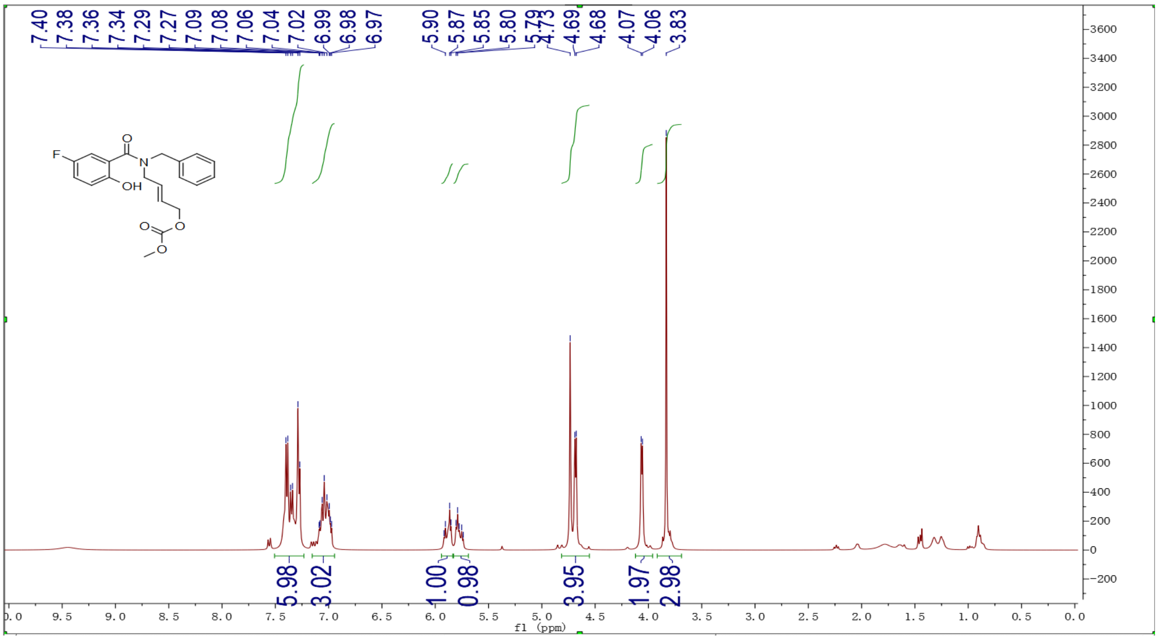


Figure 21. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 1j

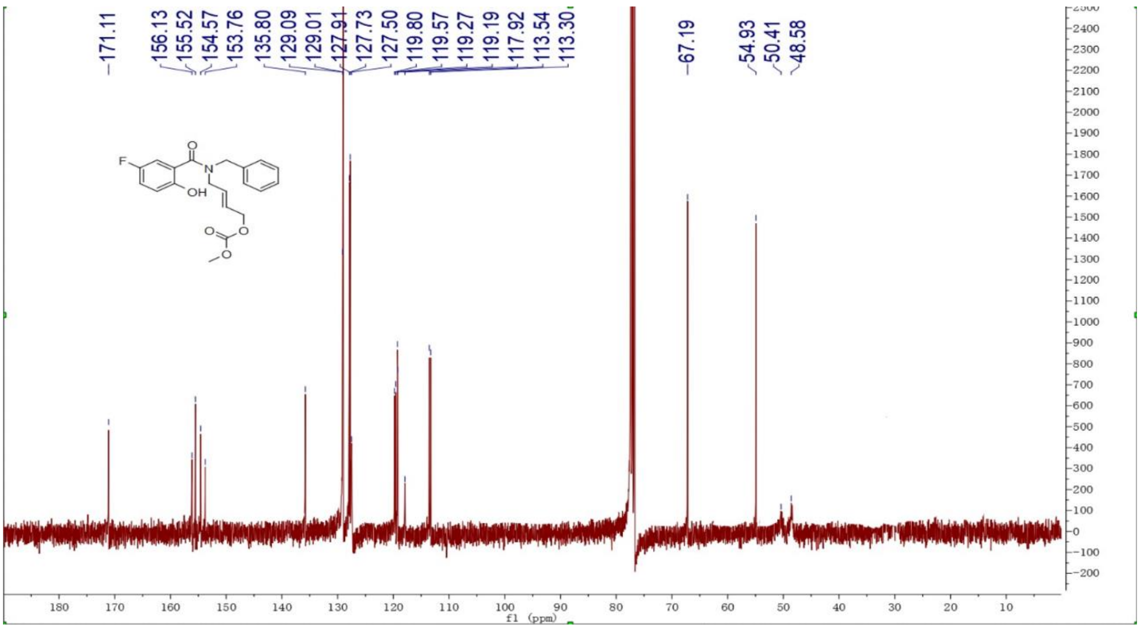


Figure 22. ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 1j

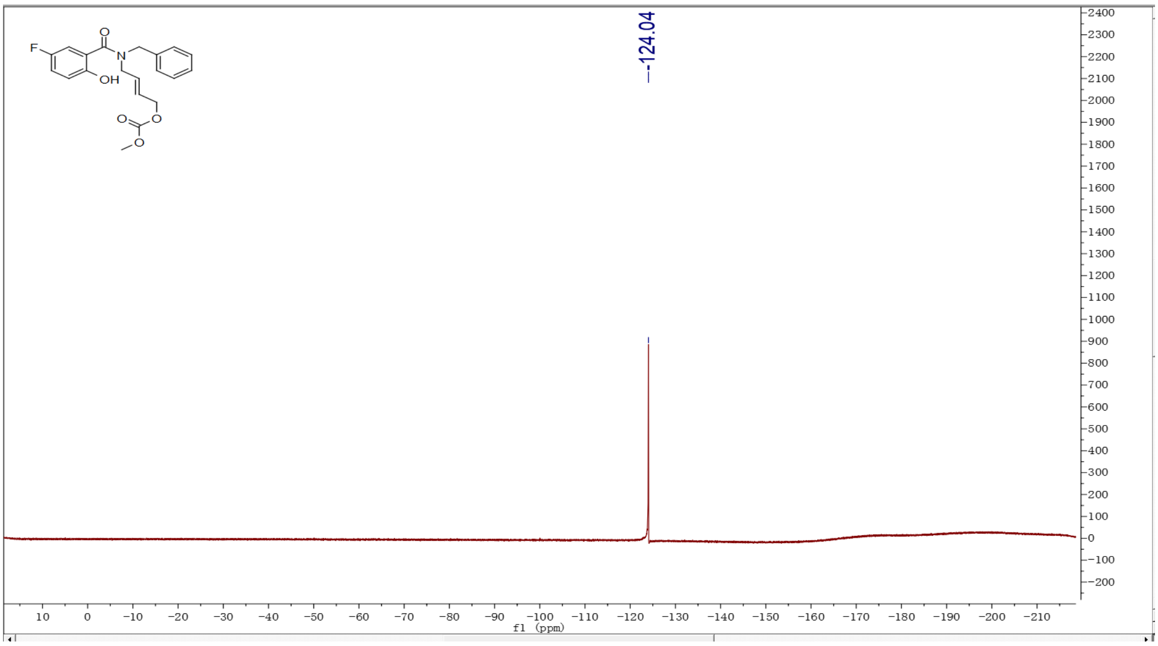


Figure 23. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1k

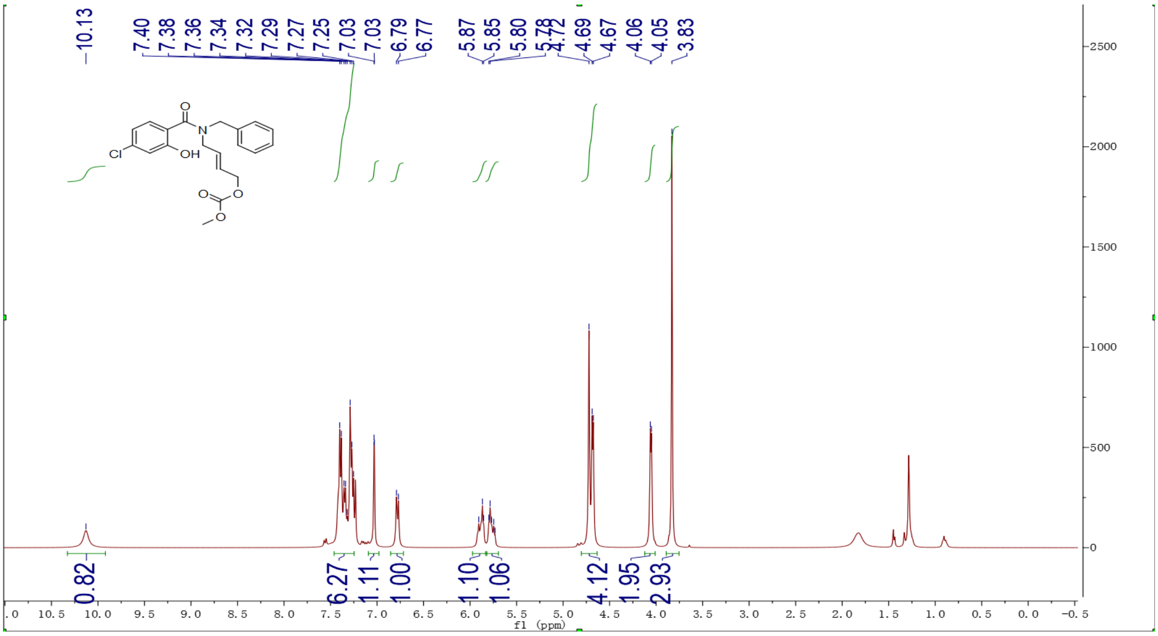


Figure 24. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 1k

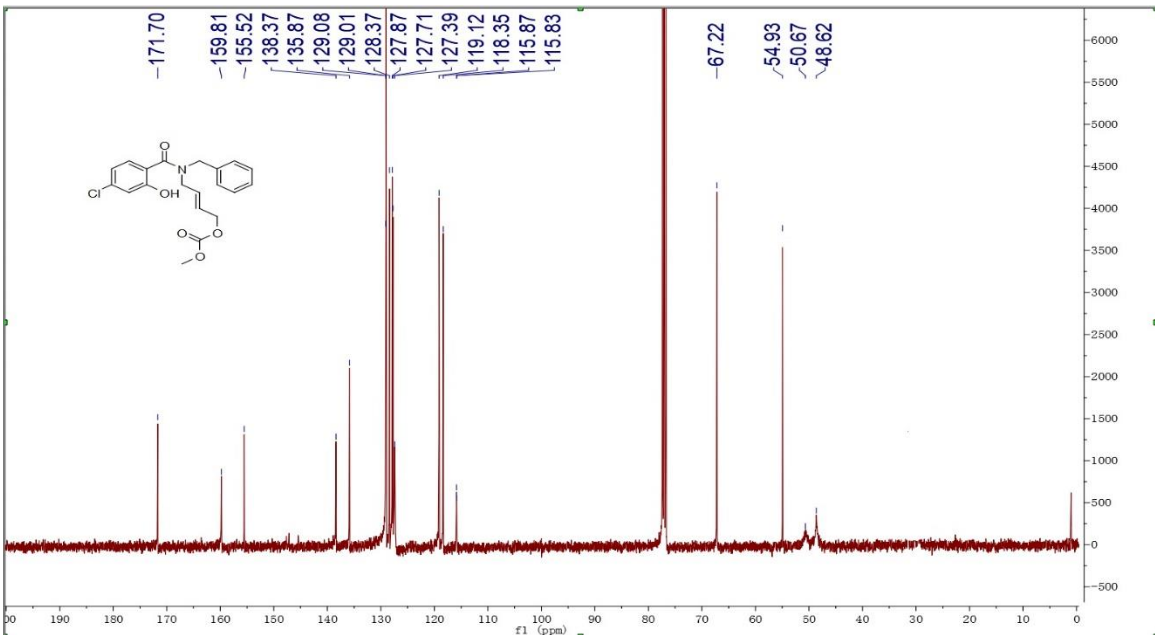


Figure 25. ^{1}**H NMR (400 MHz, CDCl$_3$) spectrum of 1l**

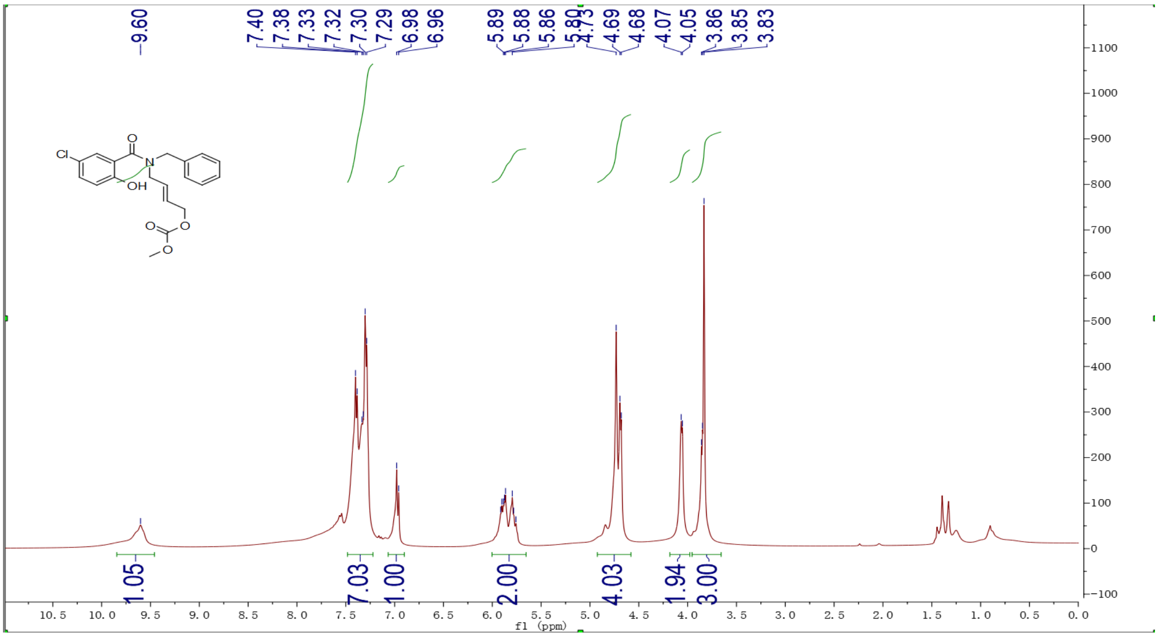


Figure 26. ^{13}**C NMR (100 MHz, CDCl$_3$) spectrum of 1l**

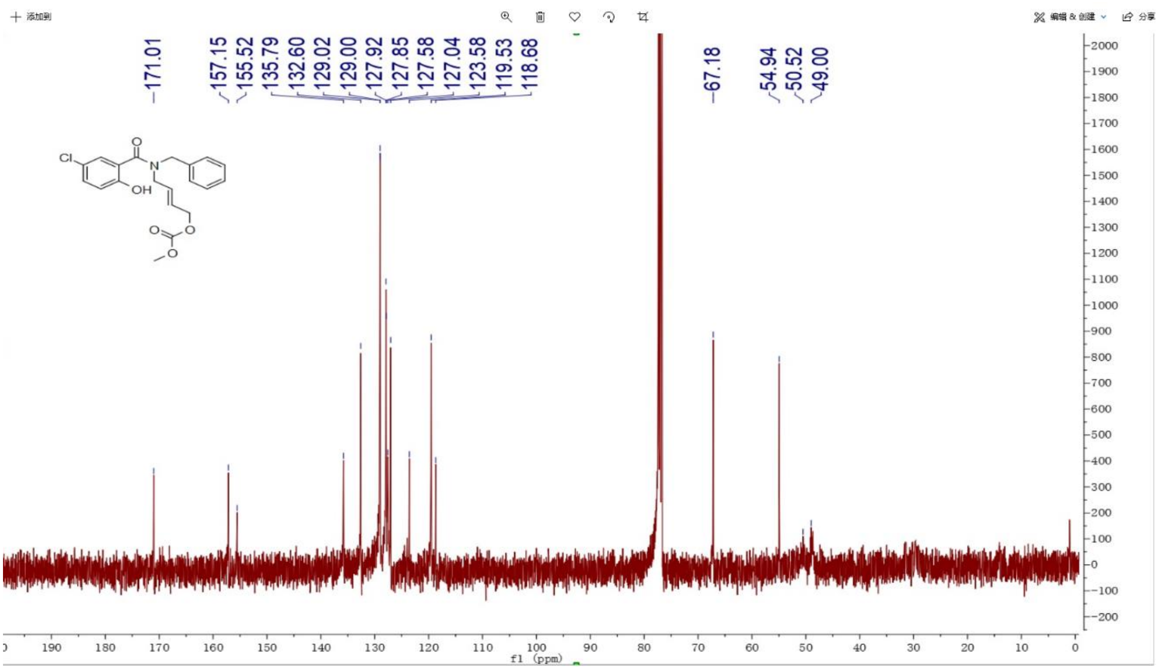


Figure 27. **[1]H NMR (400 MHz, CDCl$_3$) spectrum of 1m**

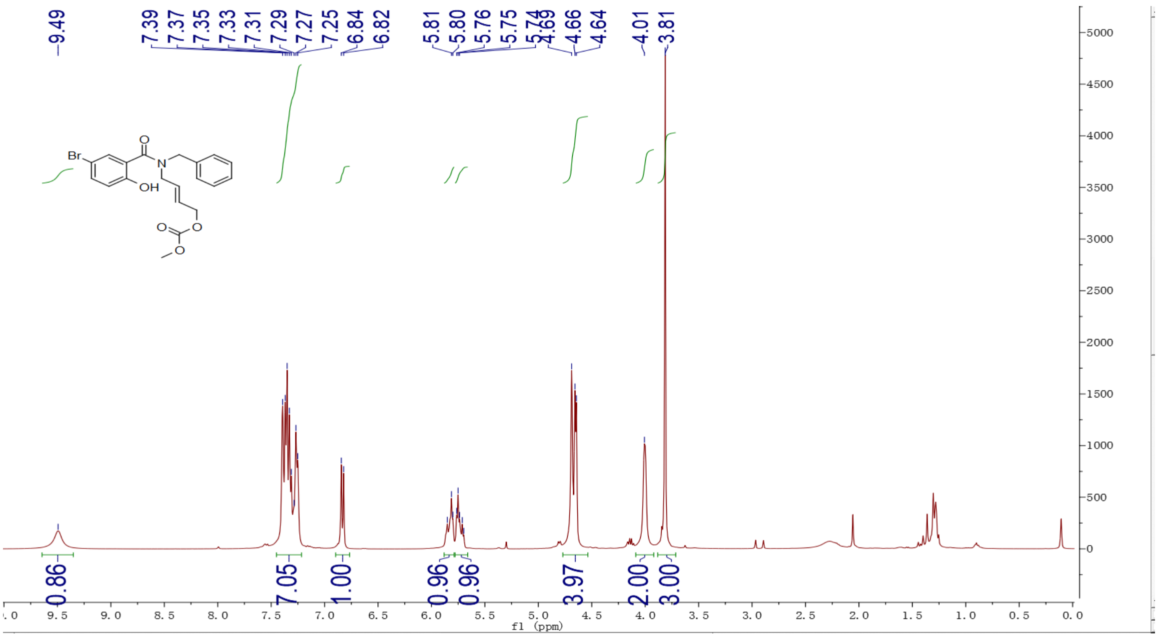


Figure 28. **[13]C NMR (100 MHz, CDCl$_3$) spectrum of 1m**

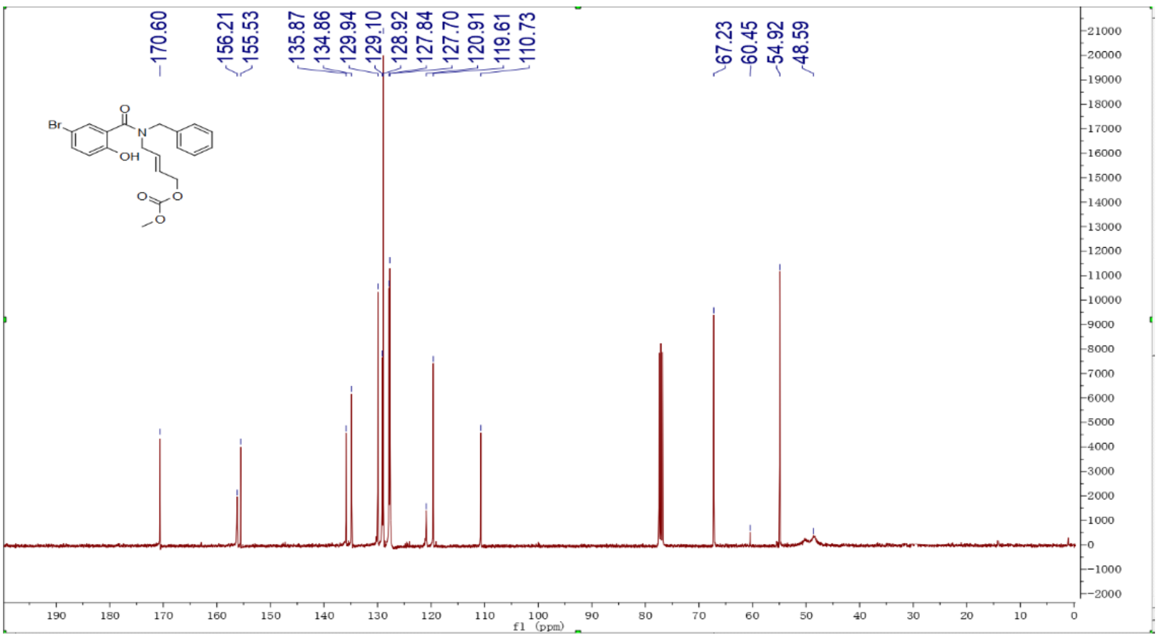


Figure 29. ^{1}H **NMR (400 MHz,** $CDCl_3$**) spectrum of 1n**

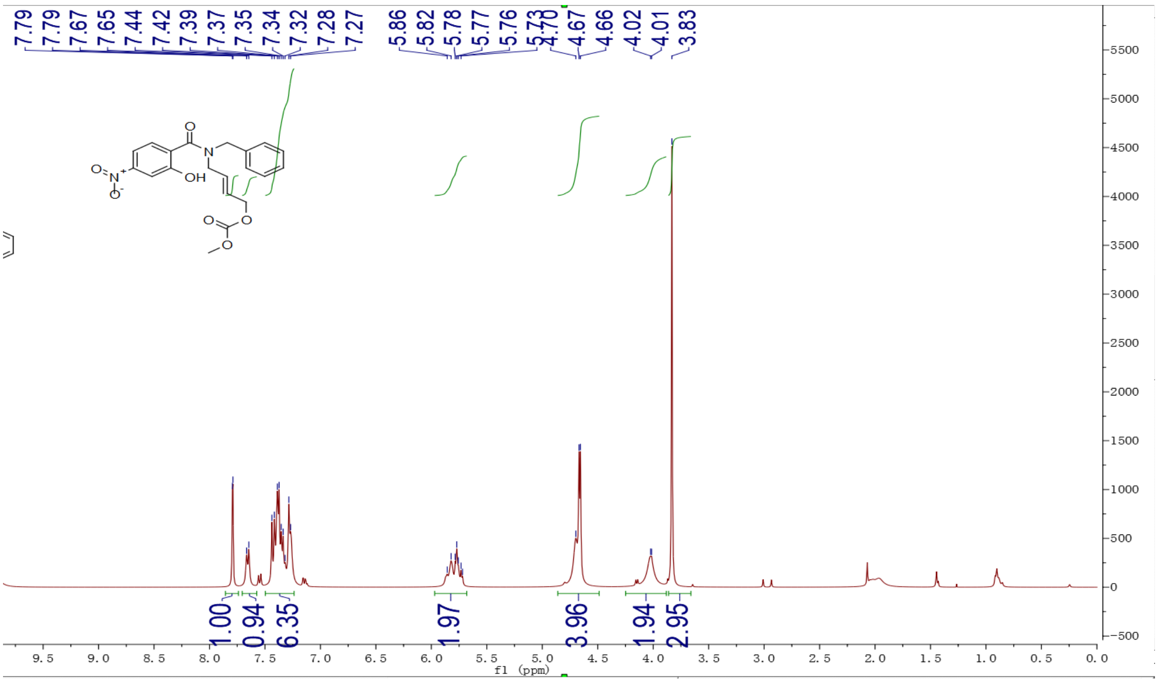


Figure 30. ^{13}C **NMR (100 MHz,** $CDCl_3$**) spectrum of 1n**

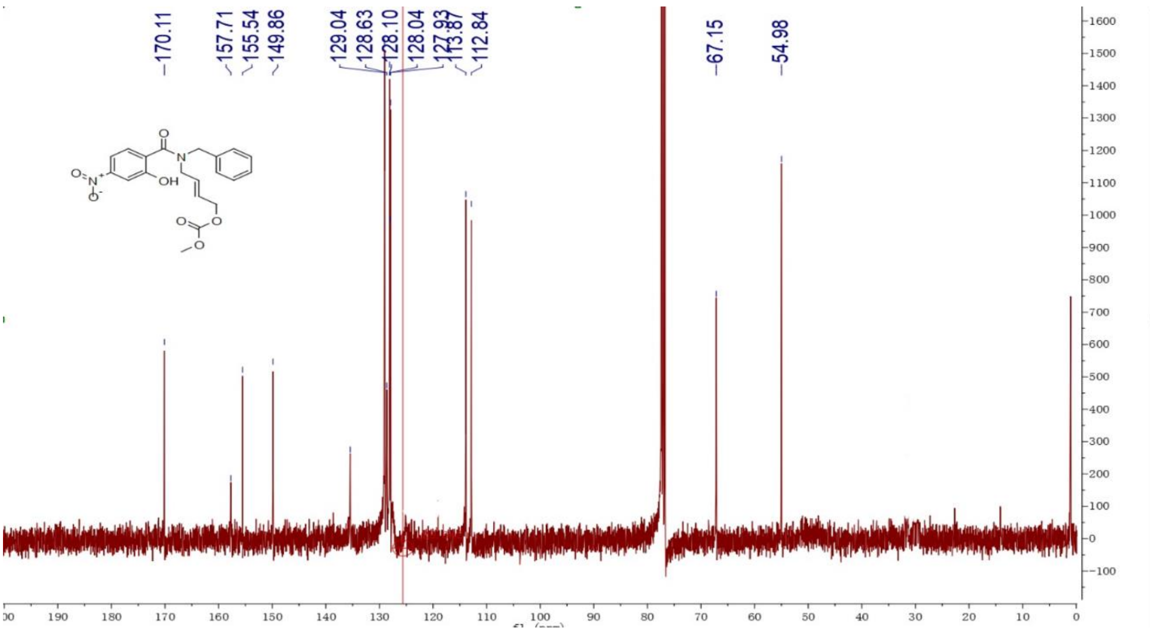


Figure 31. ^{1}**H NMR (400 MHz, CDCl$_3$) spectrum of 1o**

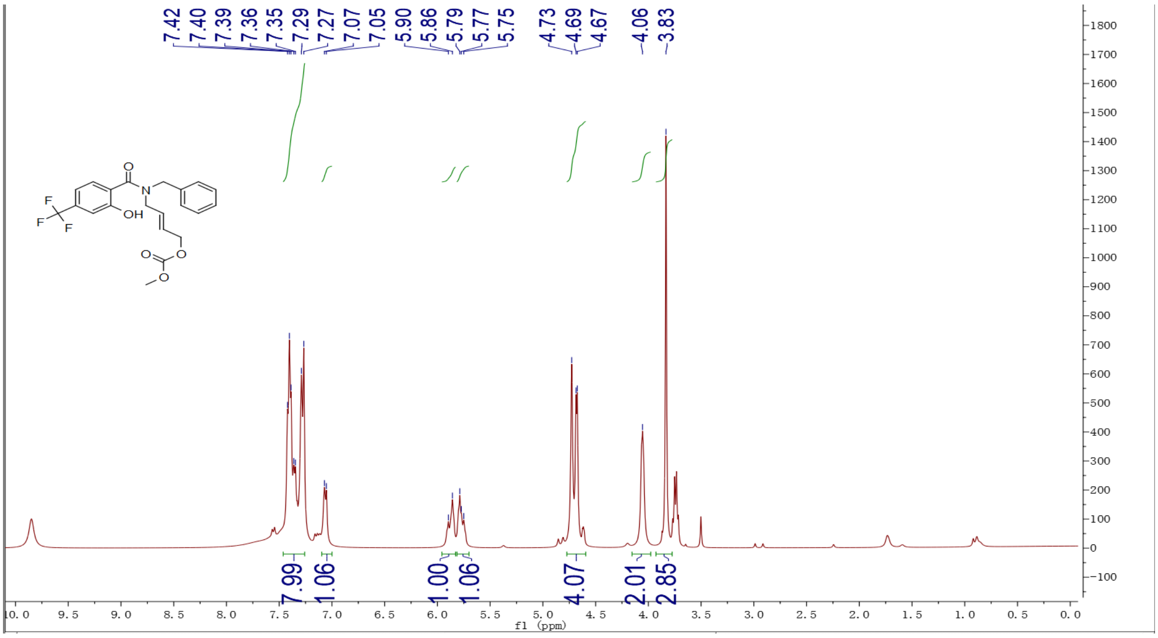


Figure 32. ^{13}**C NMR (100 MHz, CDCl$_3$) spectrum of 1o**

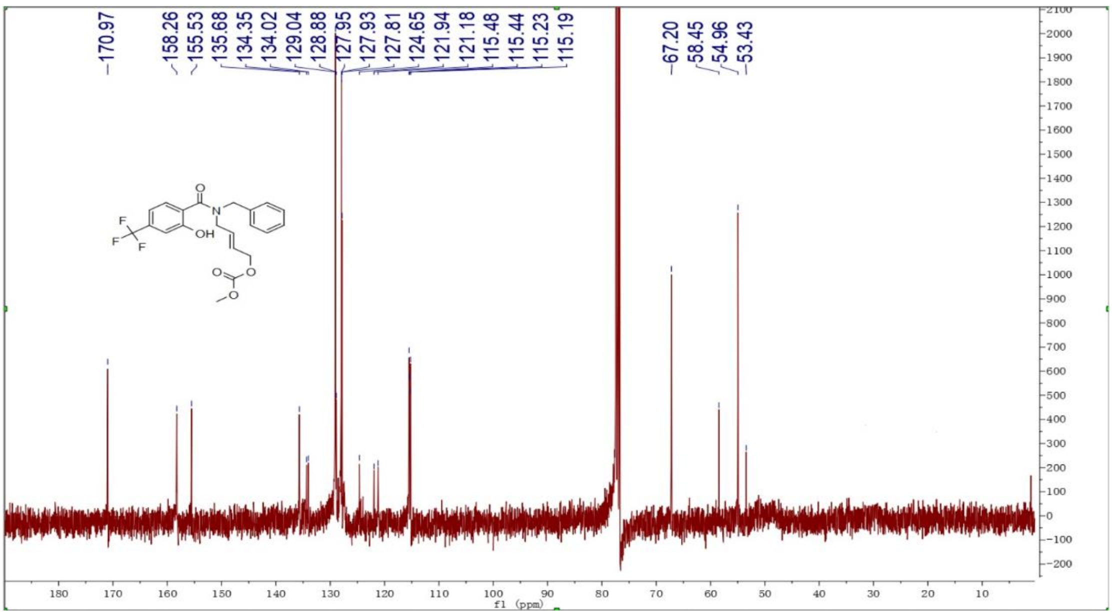


Figure 33. ^{19}**F NMR (376 MHz, CDCl$_3$) spectrum of 1o**

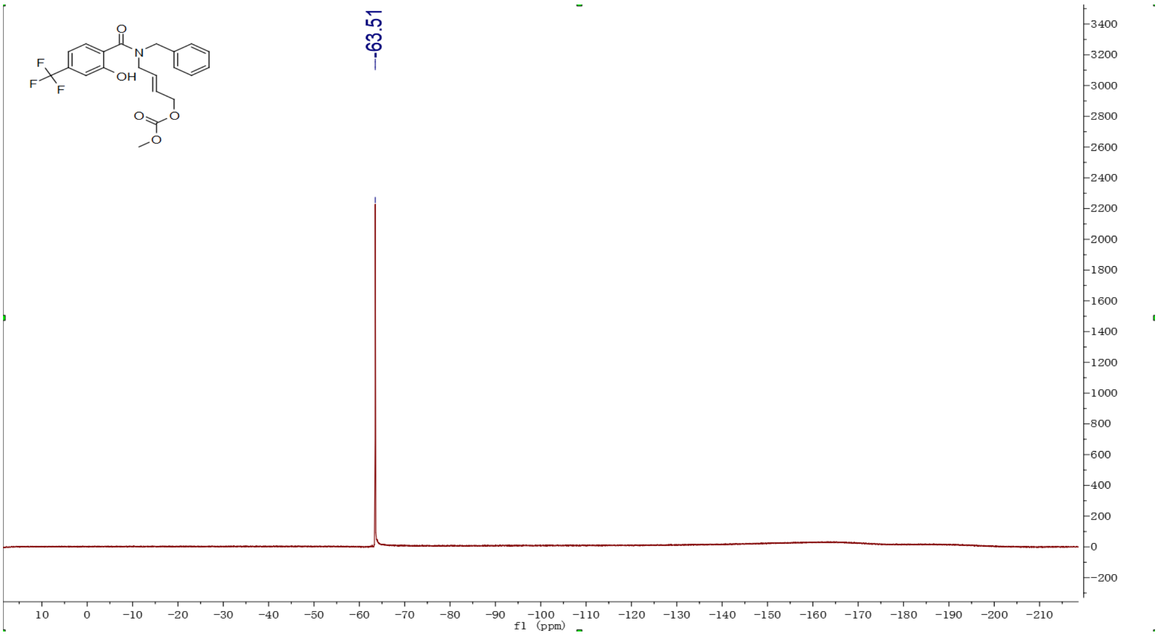


Figure 34. ^{1}**H NMR (400 MHz, CDCl$_3$) spectrum of 1p**

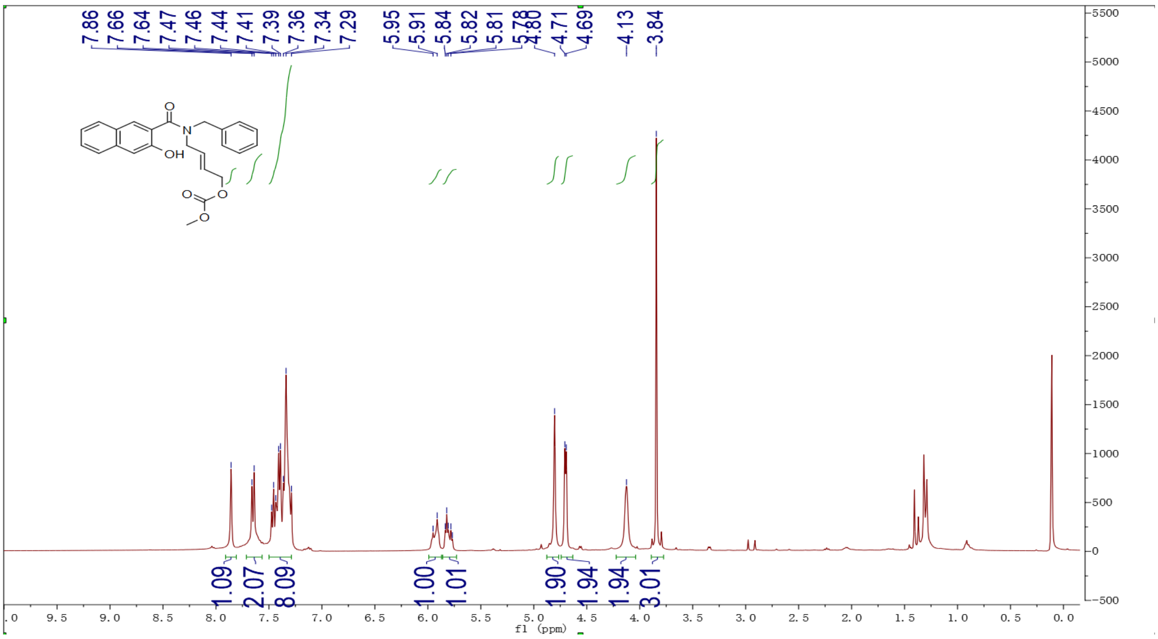


Figure 35. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 1p

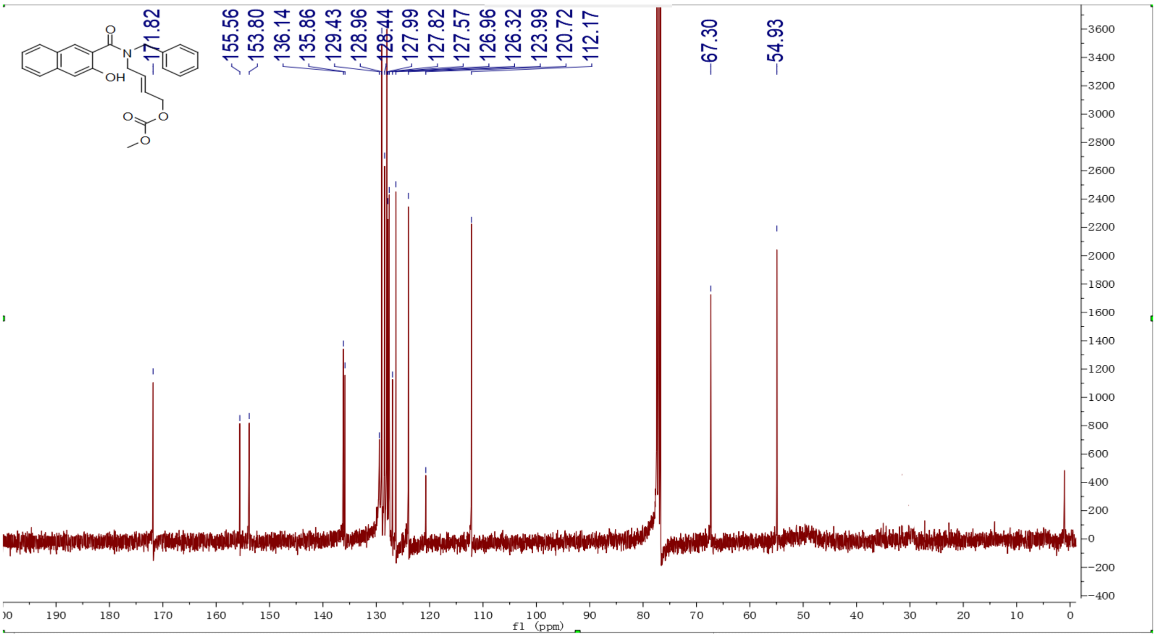


Figure 36. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1q

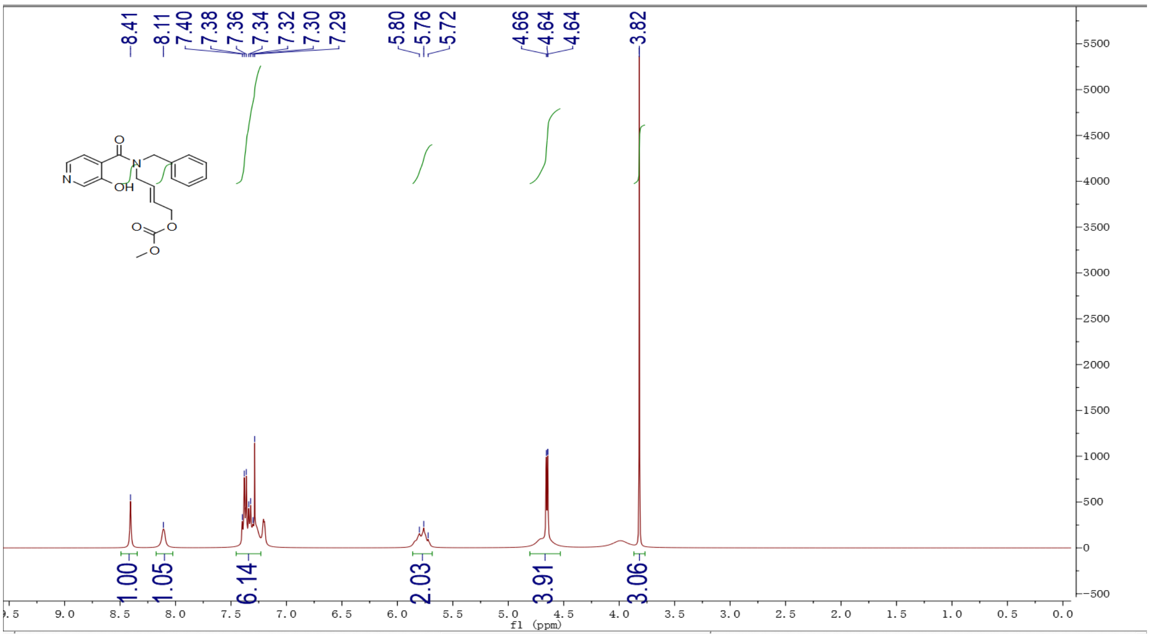


Figure 37. ^{13}**C NMR (100 MHz, CDCl$_3$) spectrum of 1q**

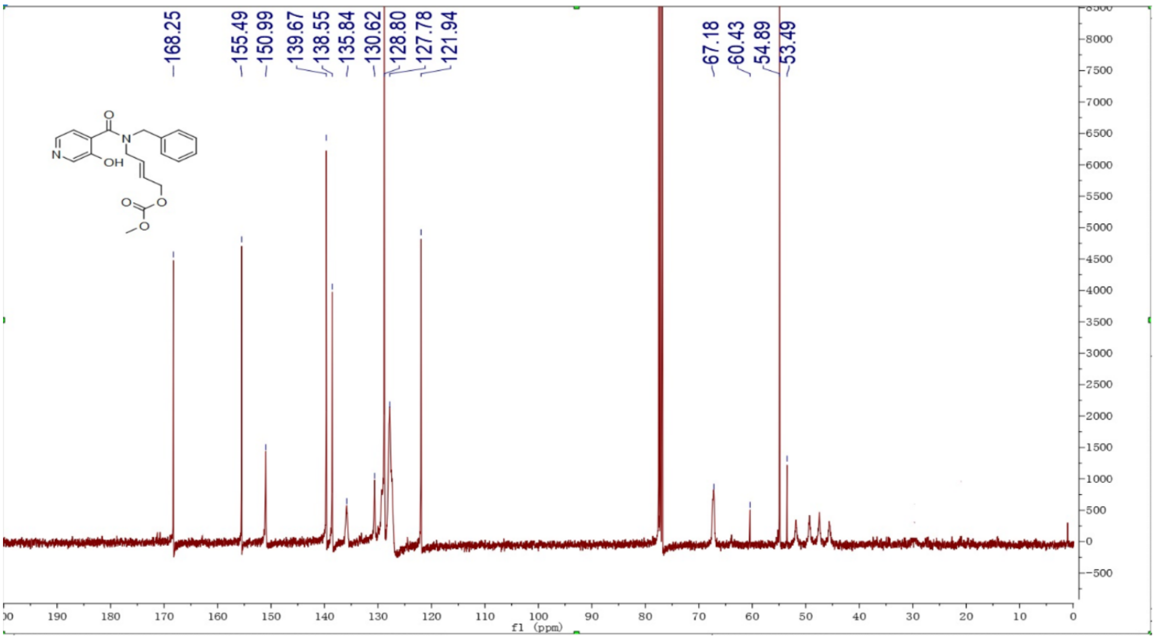


Figure 38. ^{1}**H NMR (400 MHz, CDCl$_3$) spectrum of 1r**

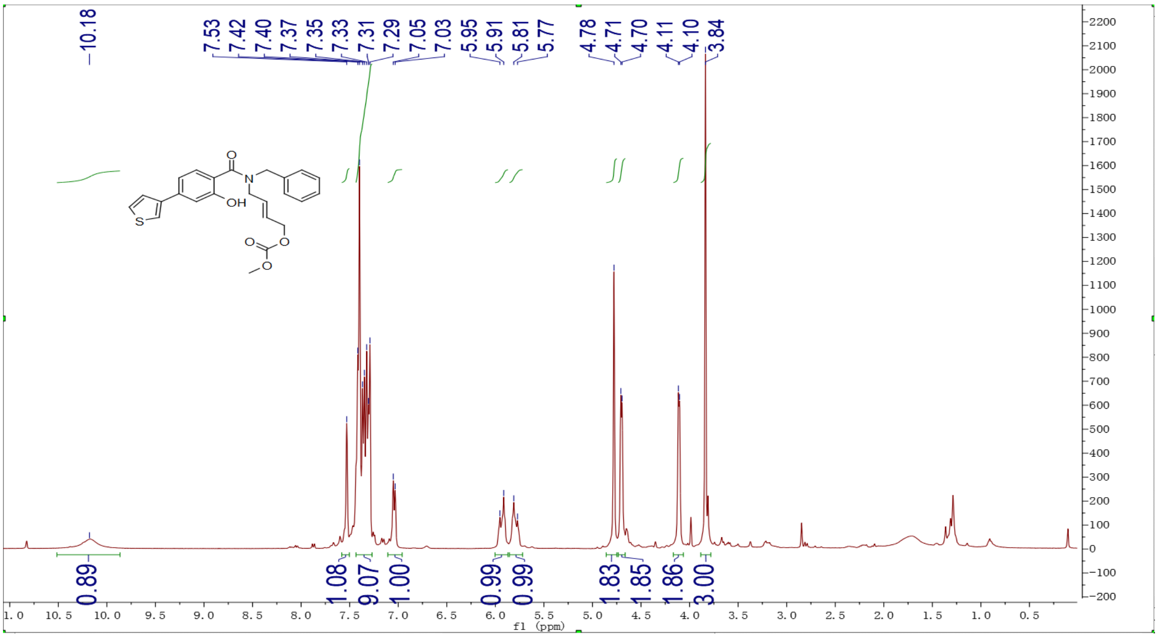


Figure 39. ^{13}C **NMR (100 MHz, $CDCl_3$) spectrum of 1r**

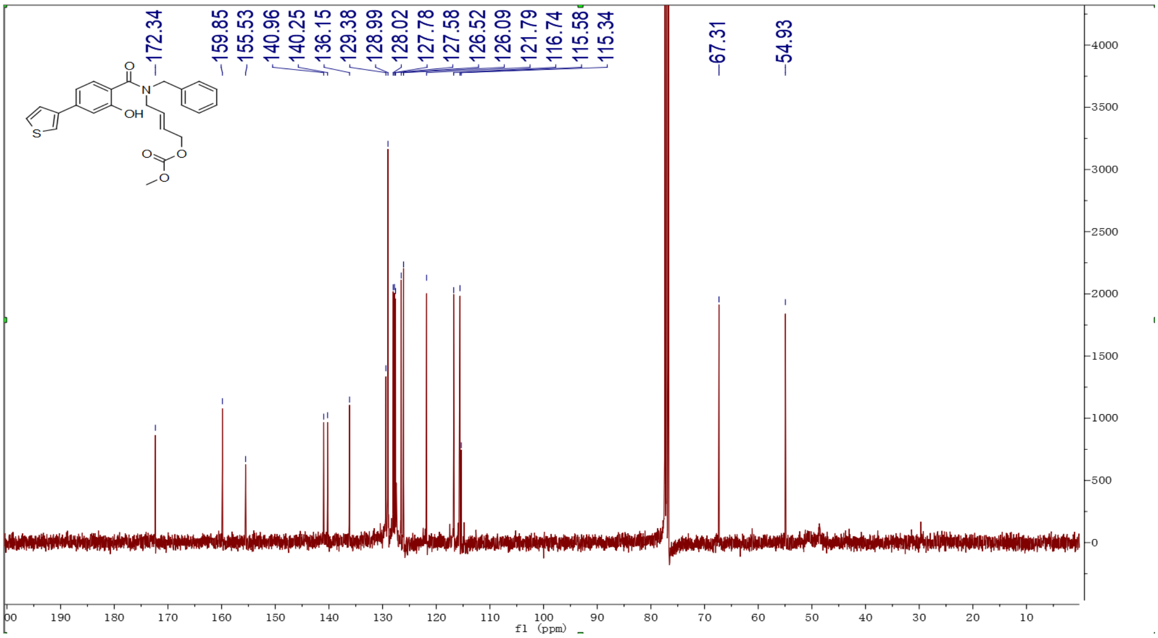


Figure 40. ^{1}H **NMR (400 MHz, $CDCl_3$) spectrum of 1s**

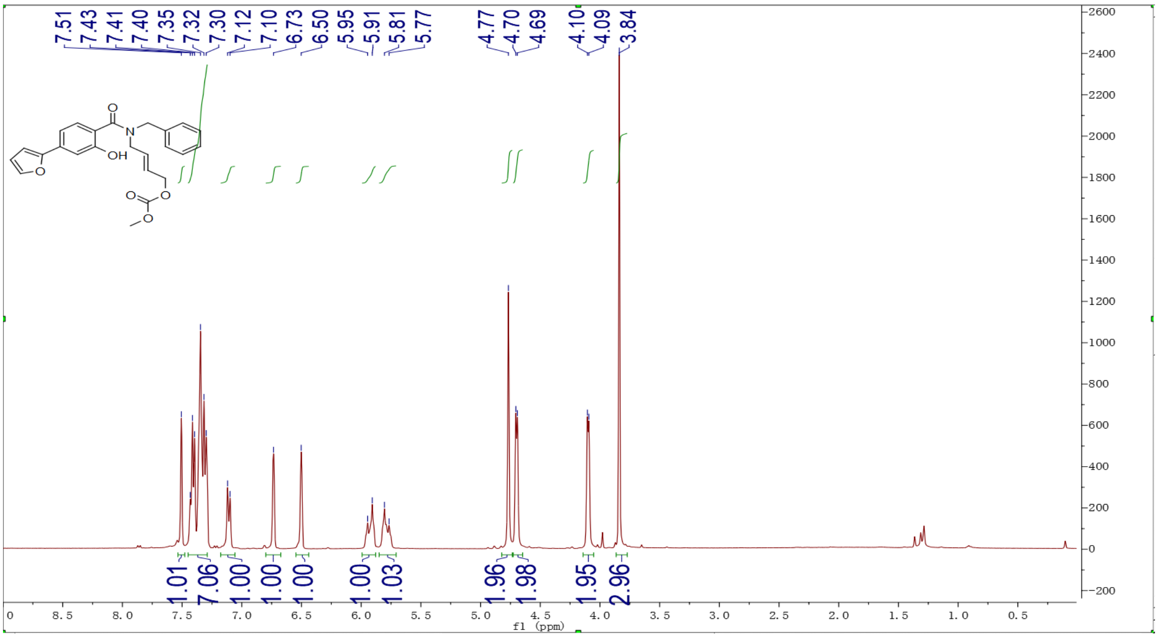


Figure 41. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 1s

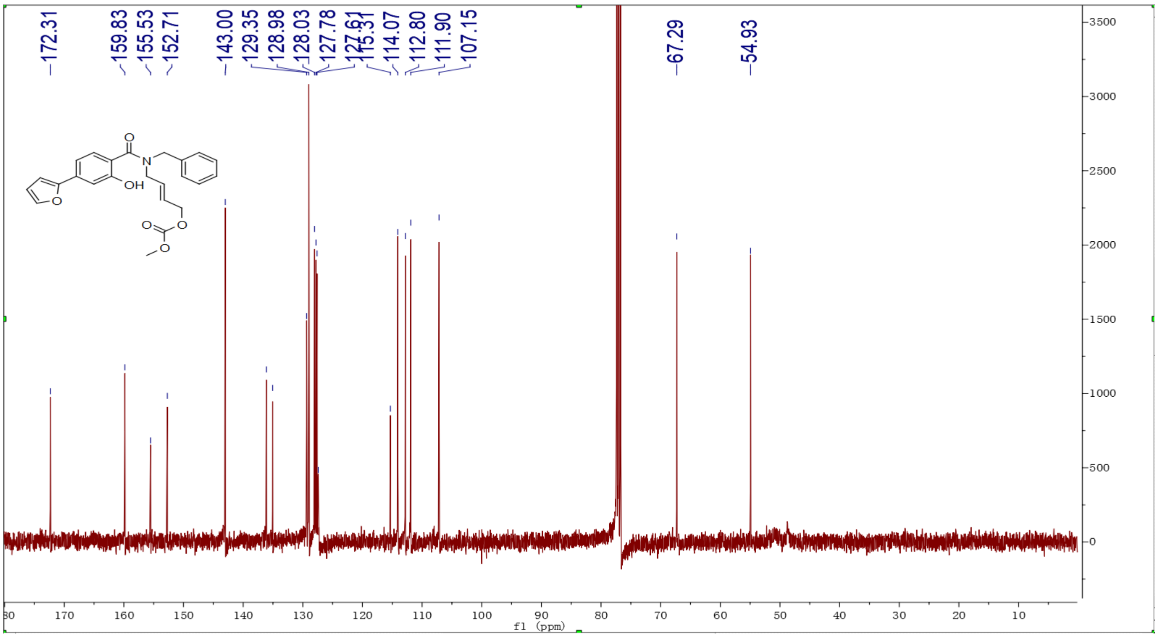


Figure 42. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1t

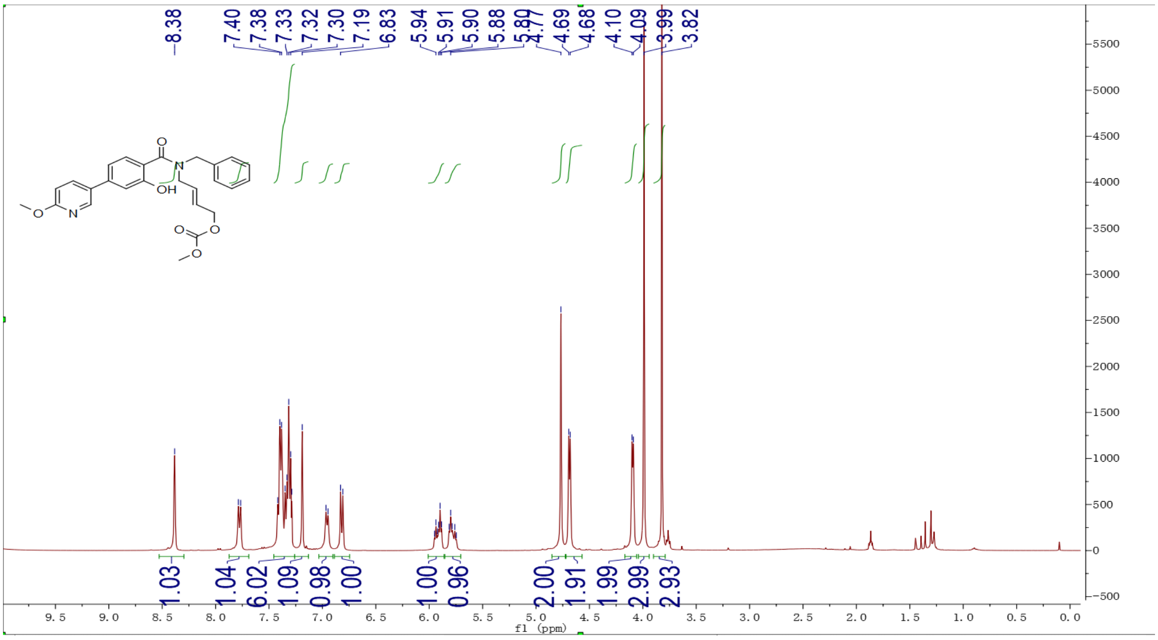


Figure 43. ^{13}**C NMR (100 MHz, CDCl$_3$) spectrum of 1t**

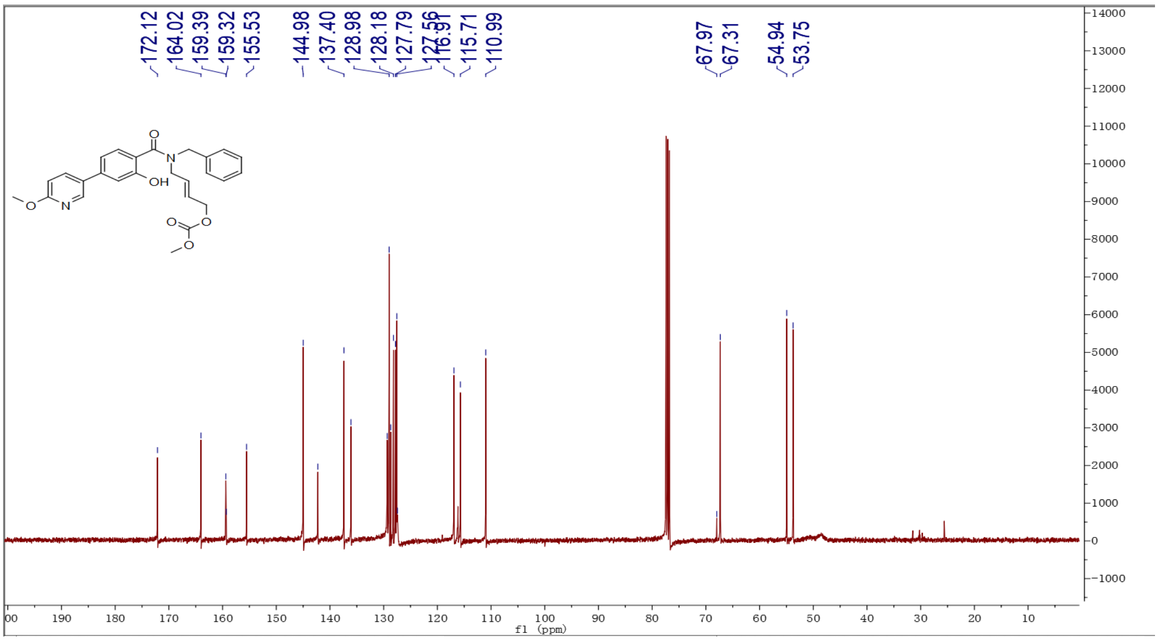


Figure 44. ^{1}**H NMR (400 MHz, CDCl$_3$) spectrum of 1u**

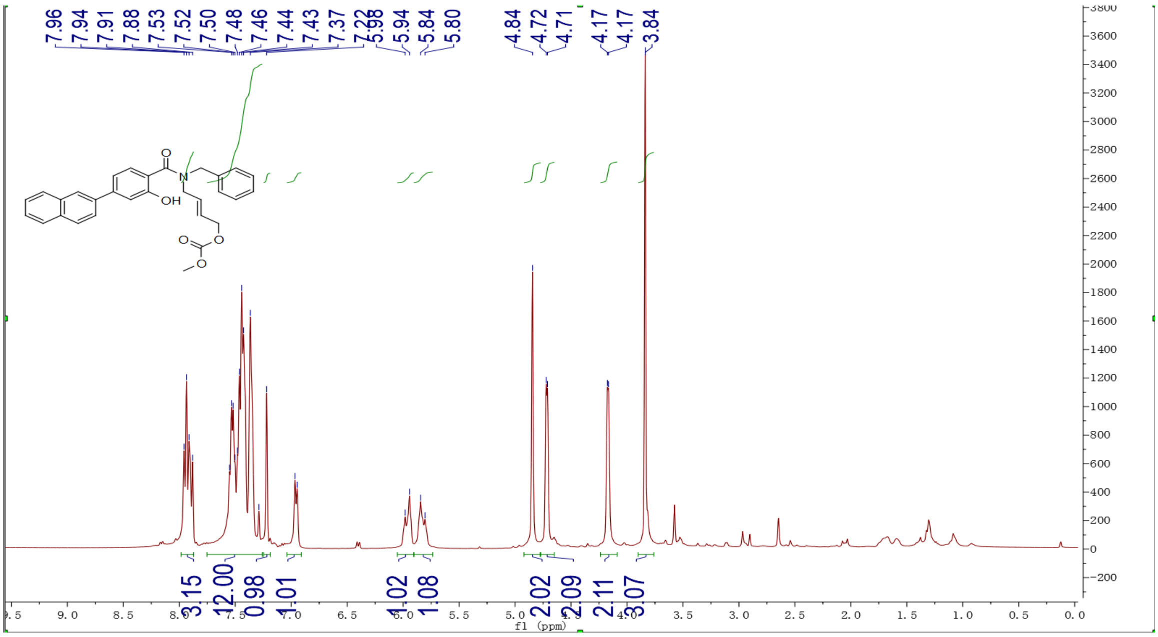


Figure 45. ^{13}**C NMR (100 MHz, CDCl$_3$) spectrum of 1u**

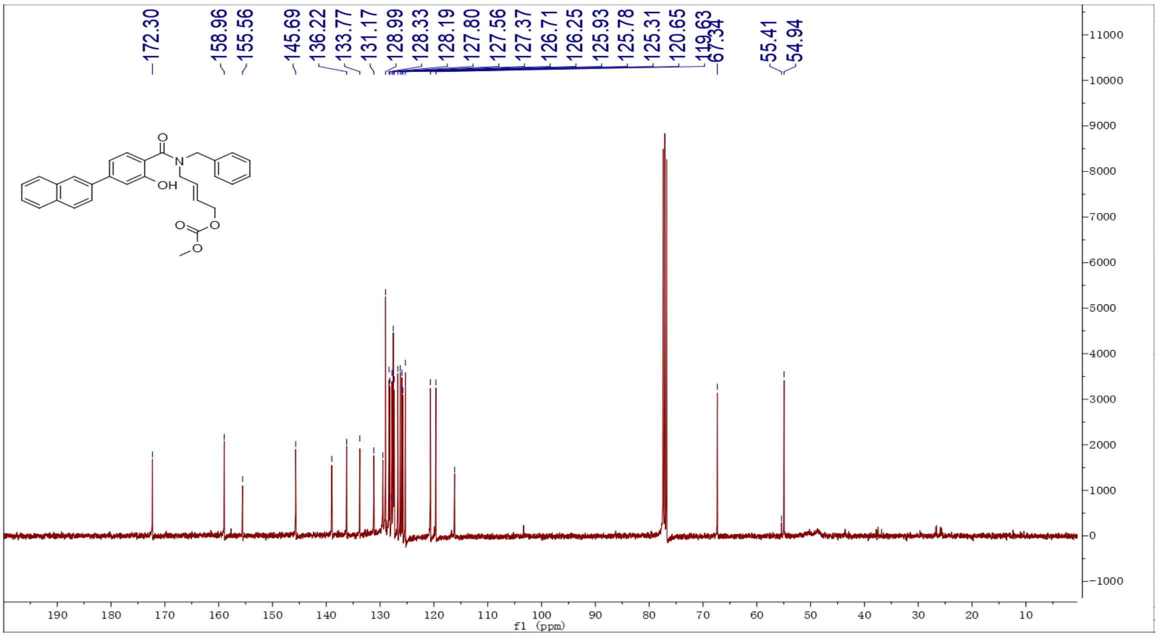


Figure 46. ^{1}**H NMR (400 MHz, CDCl$_3$) spectrum of (*E*)-1v**

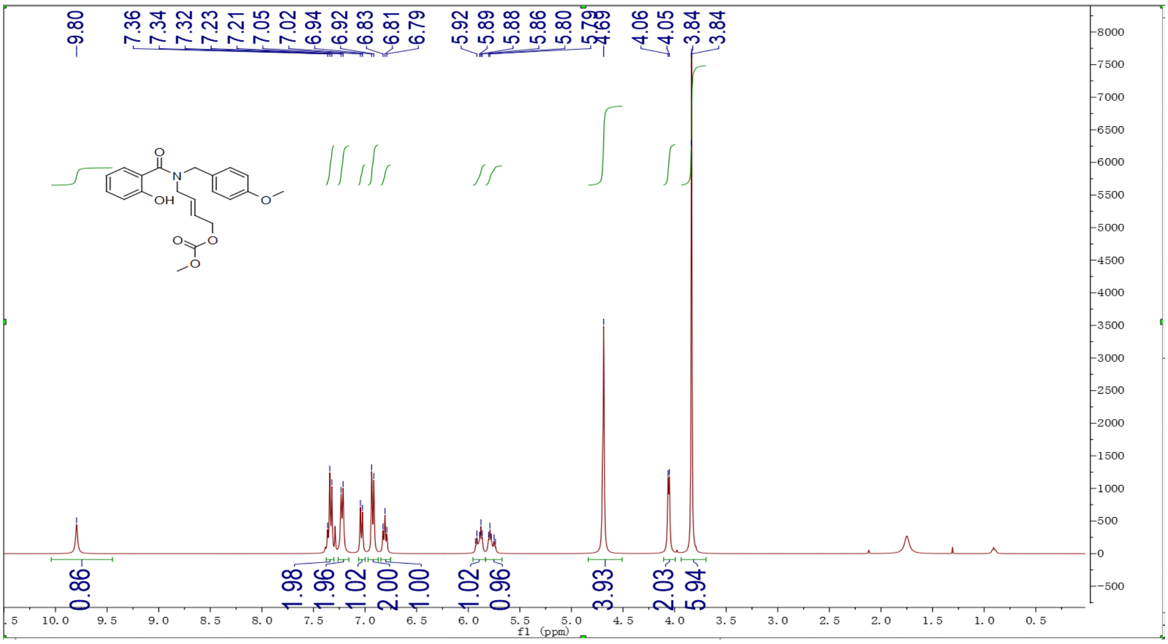


Figure 47. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*E*)-1v

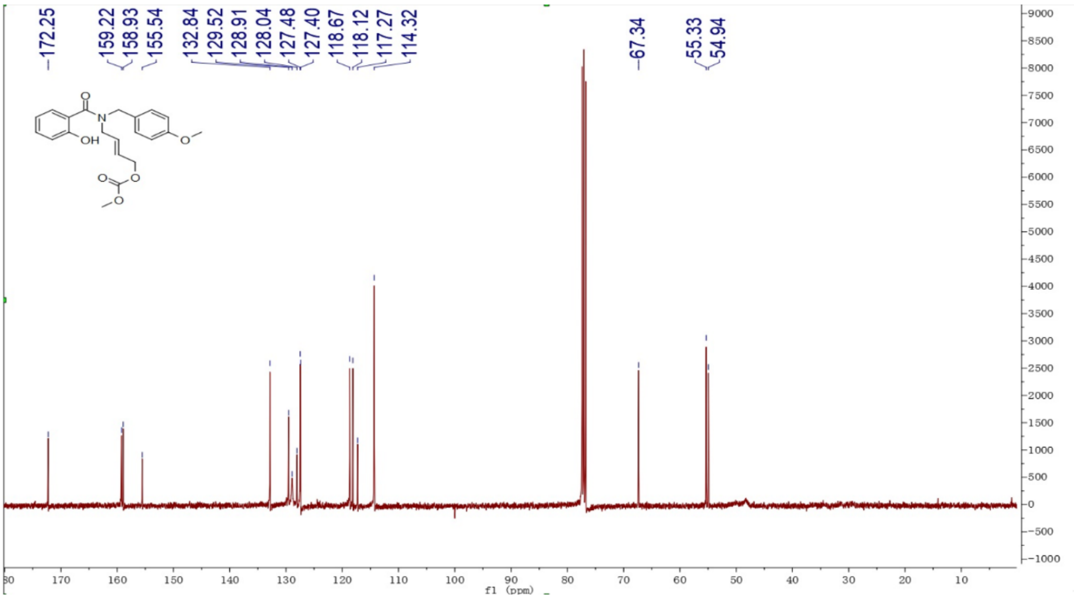


Figure 48. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*Z*)-1v

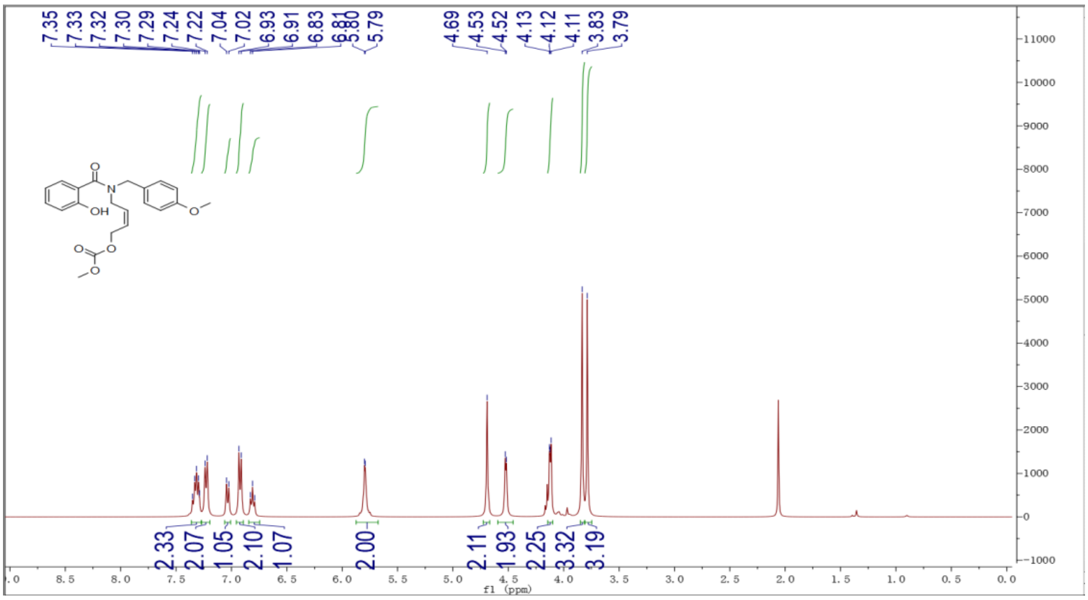
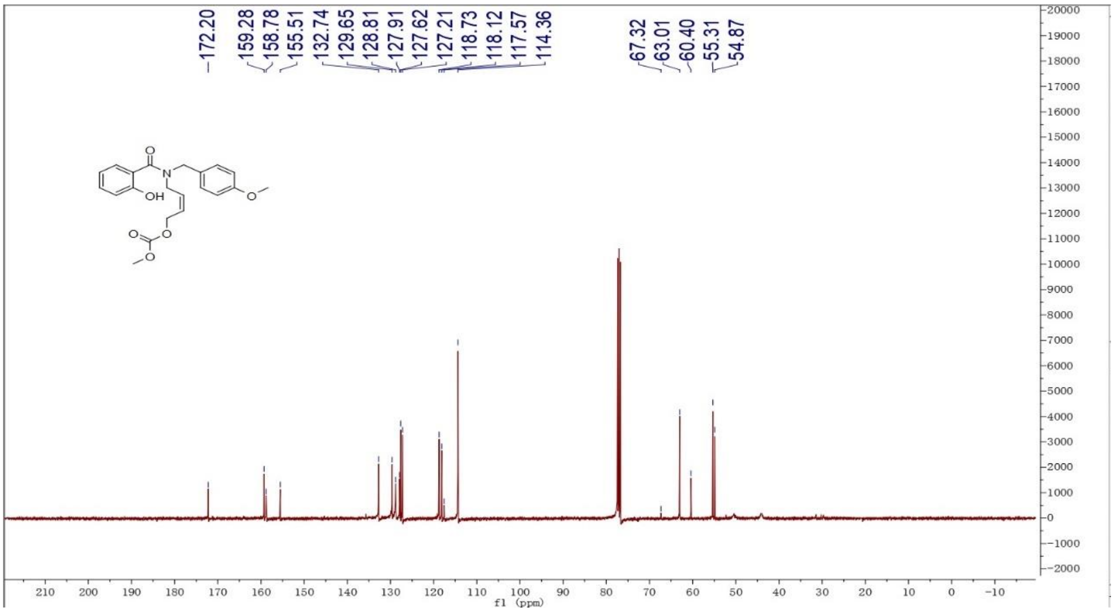


Figure 49. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*Z*)-1v



4-Benzyl-2-vinyl-3,4-dihydro-2λ^3-benzo[*f*][1,4]oxazepin-5(2*H*)-one (2a)

Figure 50. ^1H NMR (400 MHz, $CDCl_3$) spectrum of 2a

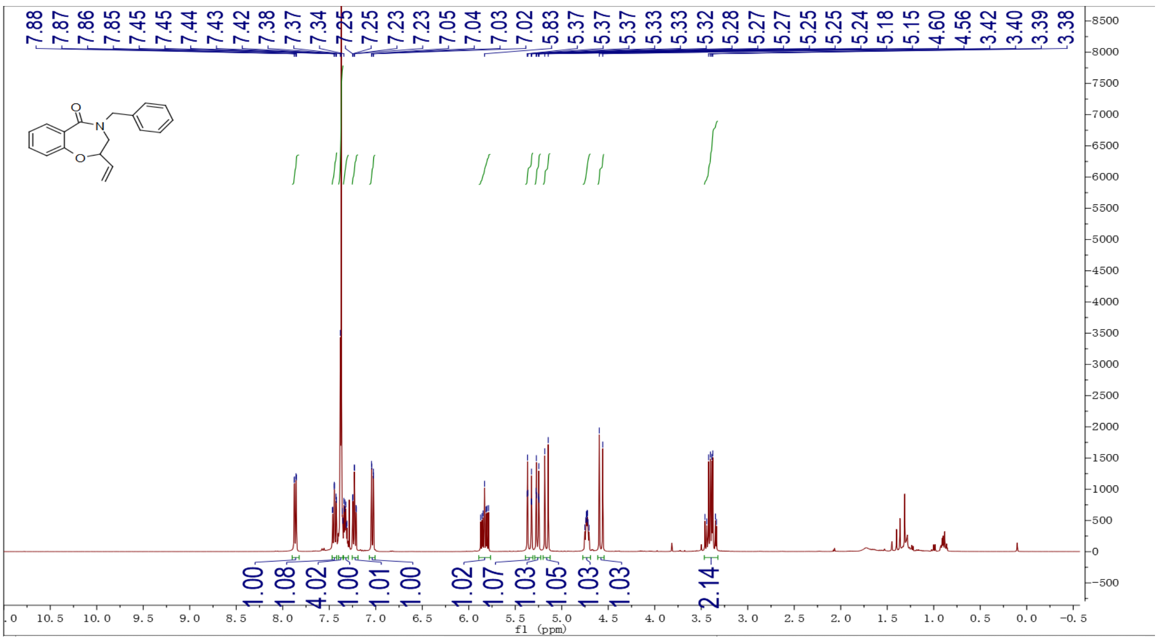
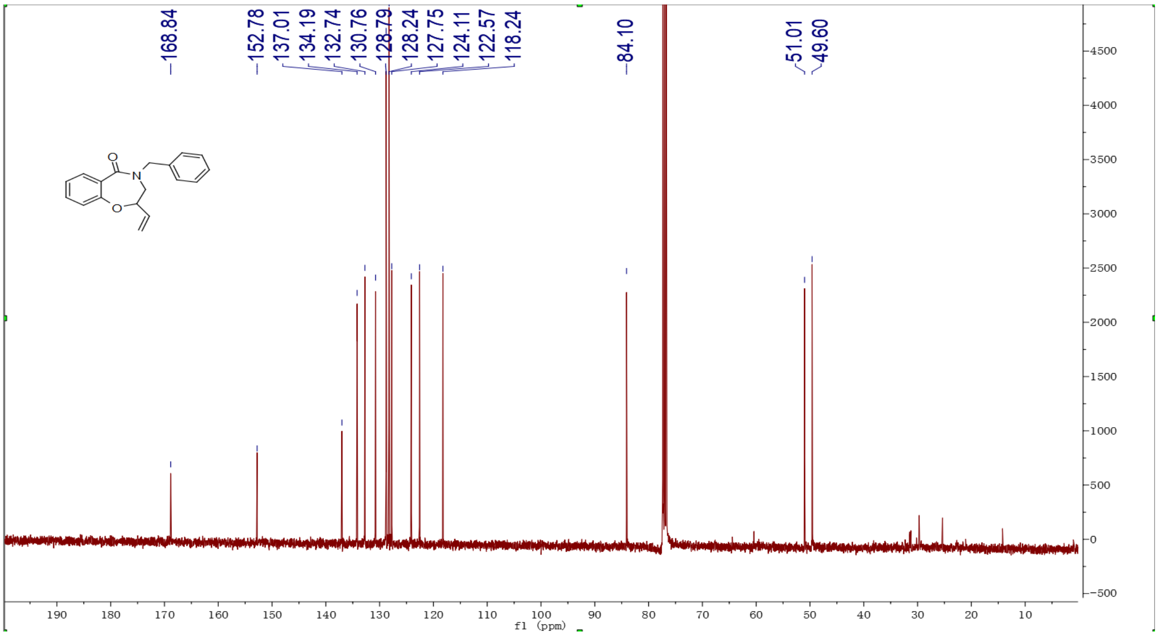


Figure 51. ^{13}**C NMR (100 MHz, CDCl$_3$) spectrum of 2a**



4-Benzyl-8-methyl-2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (2b)

Figure 52. ^{1}**H NMR (400 MHz, CDCl$_3$) spectrum of 2b**

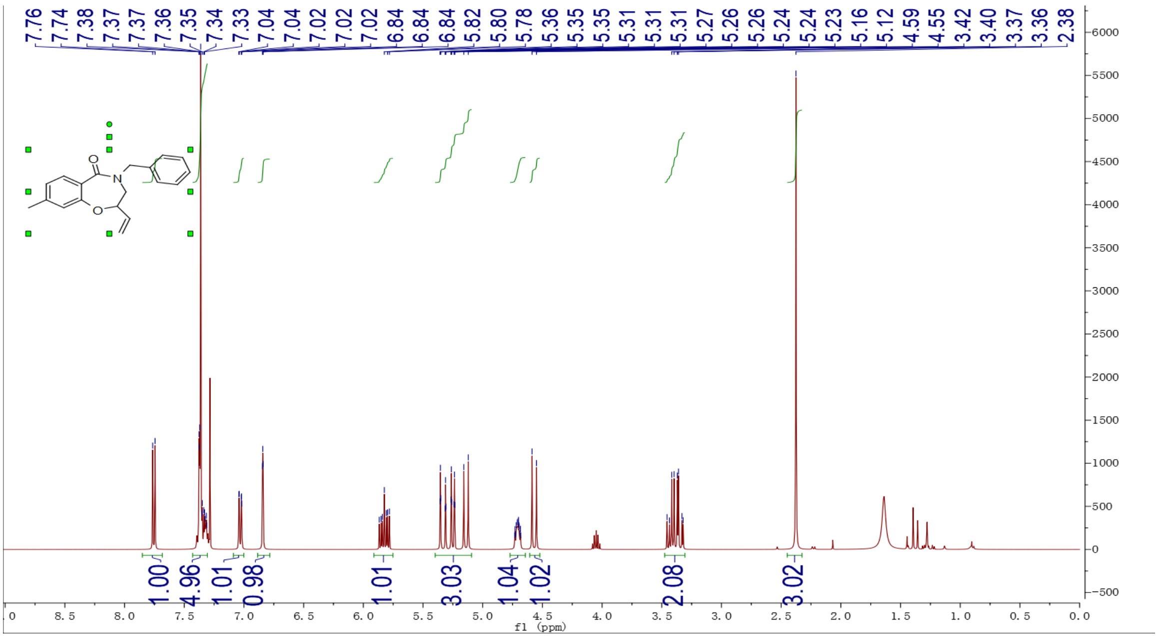
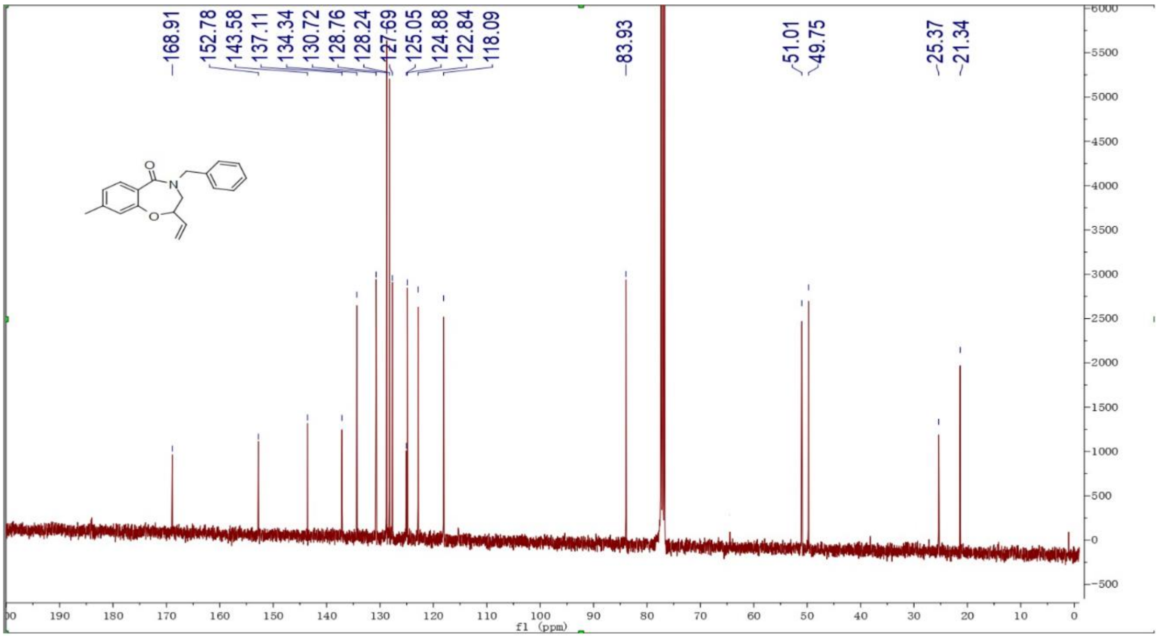


Figure 53. ^{13}C NMR (100 MHz, CDCl$_3$) spectrum of 2b



4-Benzyl-7-methyl-2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (2c)

Figure 54. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of 2c

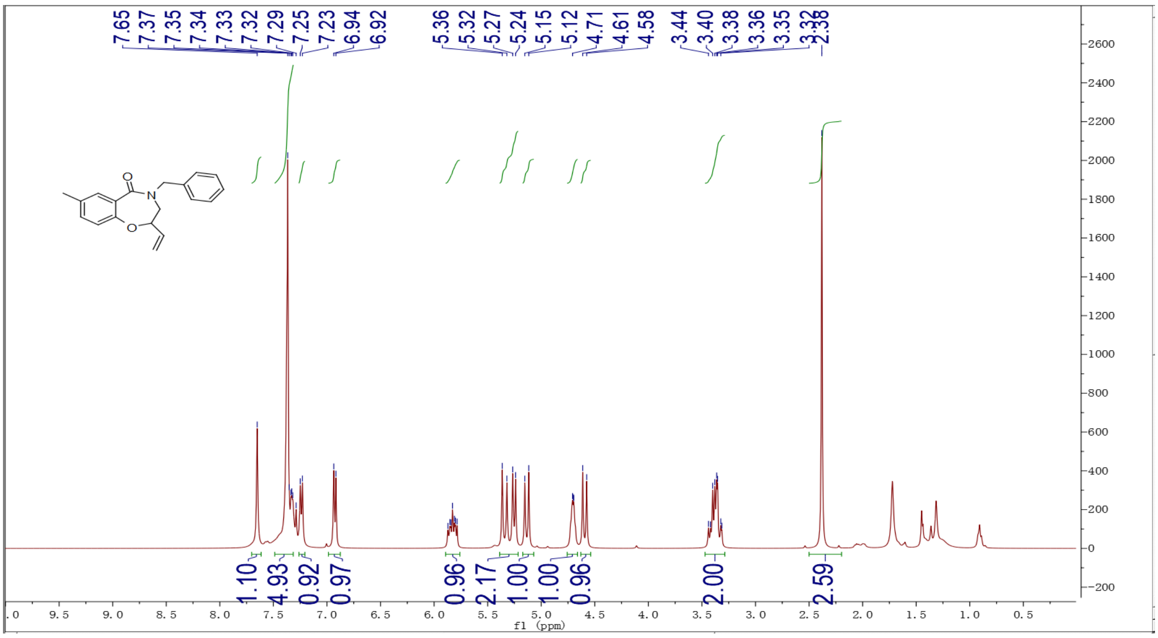
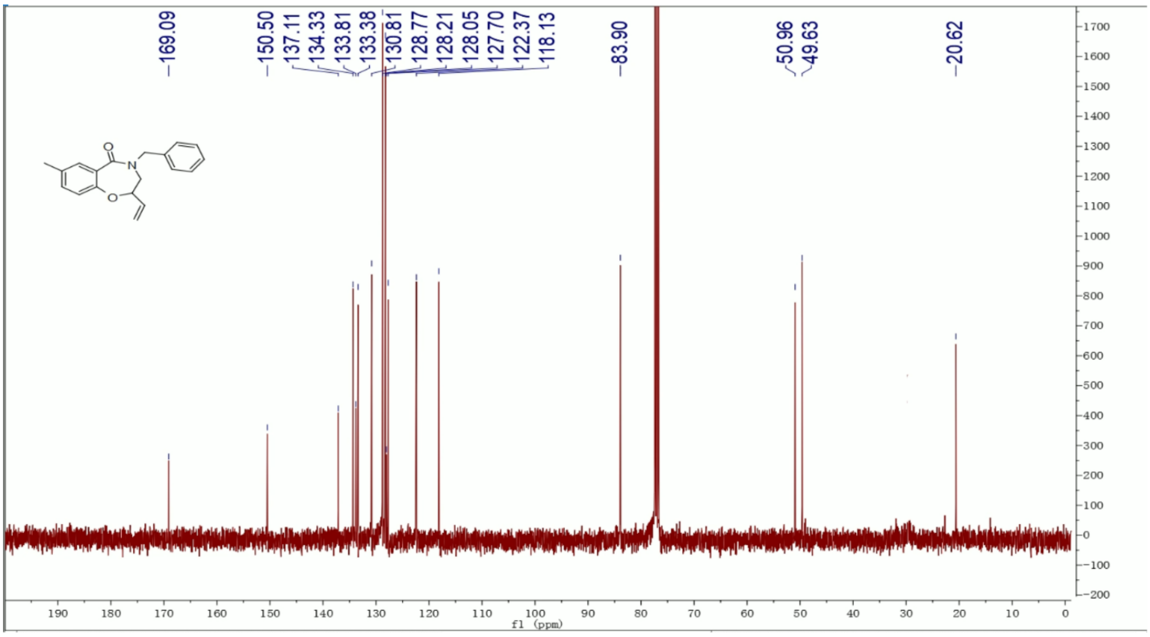


Figure 55. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2c



4-Benzyl-6-methyl-2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (2d)

Figure 56. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2d

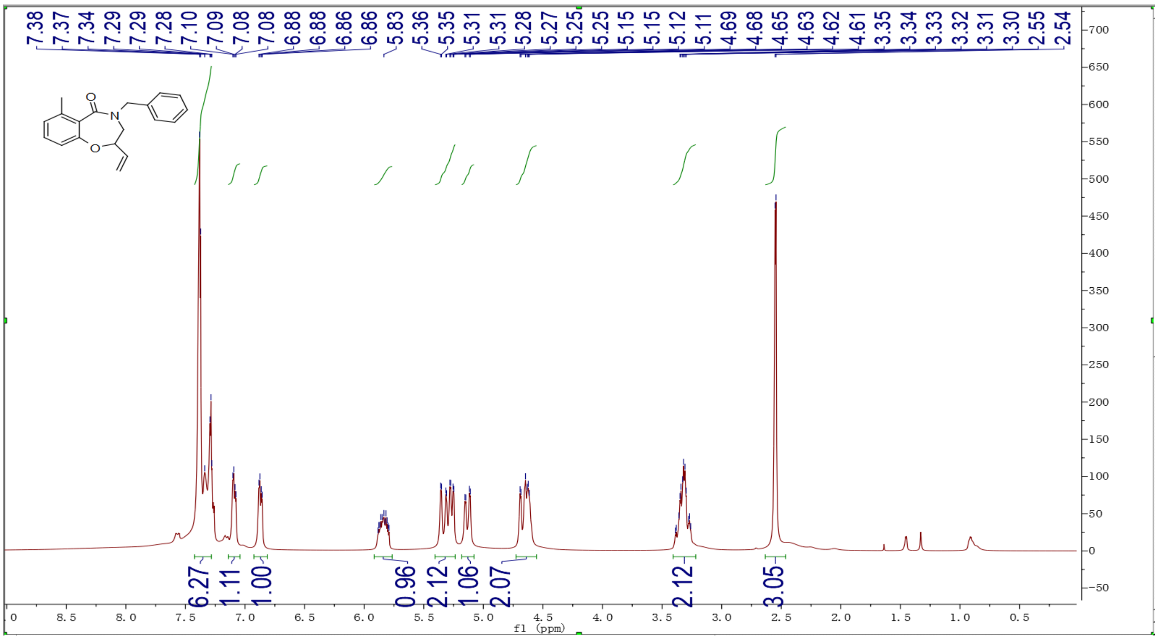
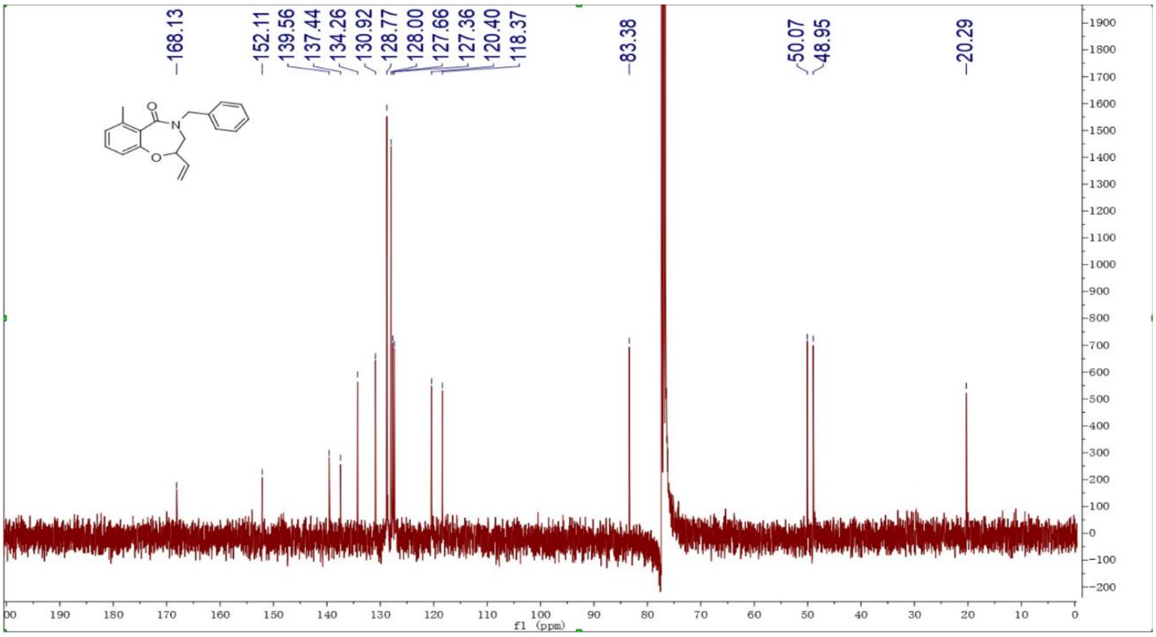


Figure 57. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2d



4-Benzyl-9-methoxy-2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (2e)

Figure 58. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2e

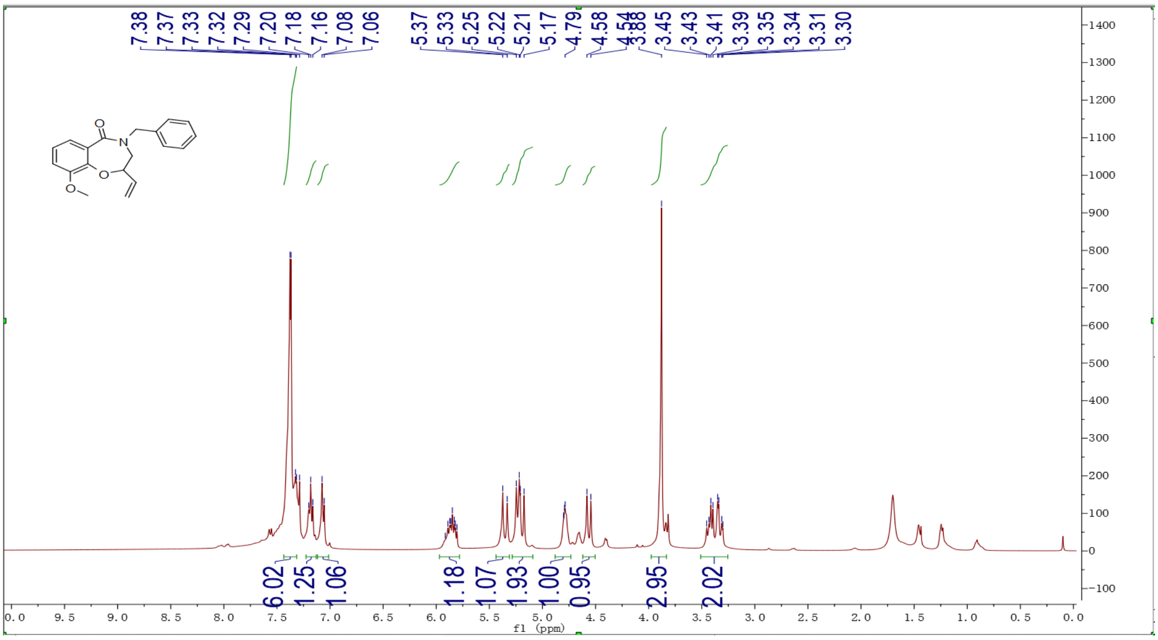
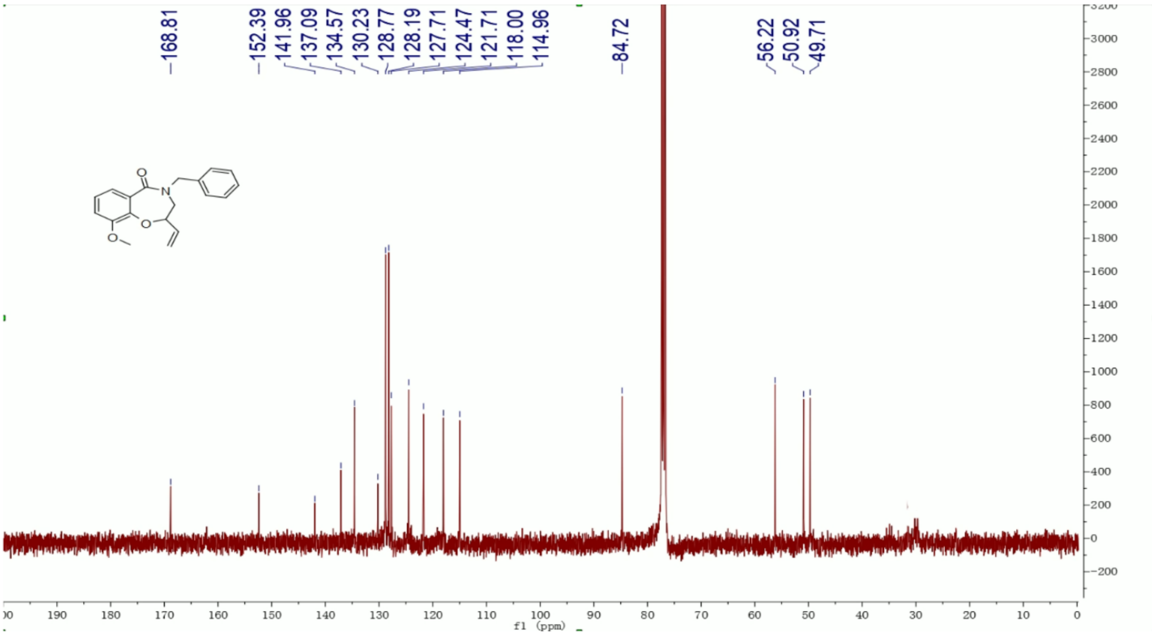


Figure 59. ^{13}**C NMR (100 MHz, CDCl$_3$) spectrum of 2e**



4-Benzyl-8-methoxy-2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (2f)

Figure 60. ^{1}**H NMR (400 MHz, CDCl$_3$) spectrum of 2f**

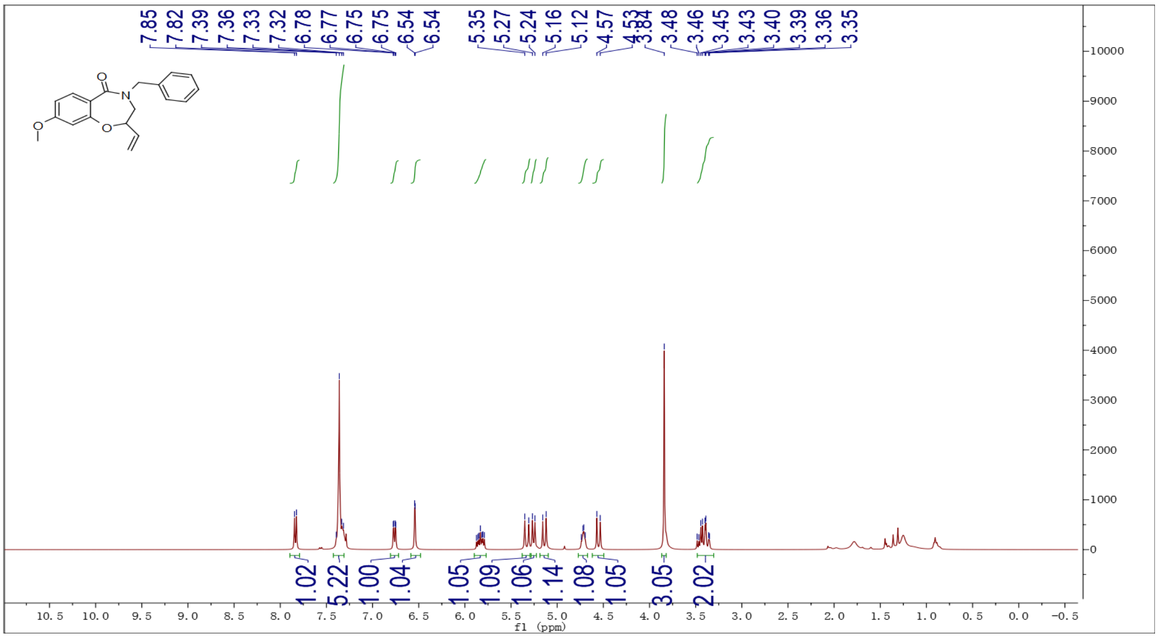
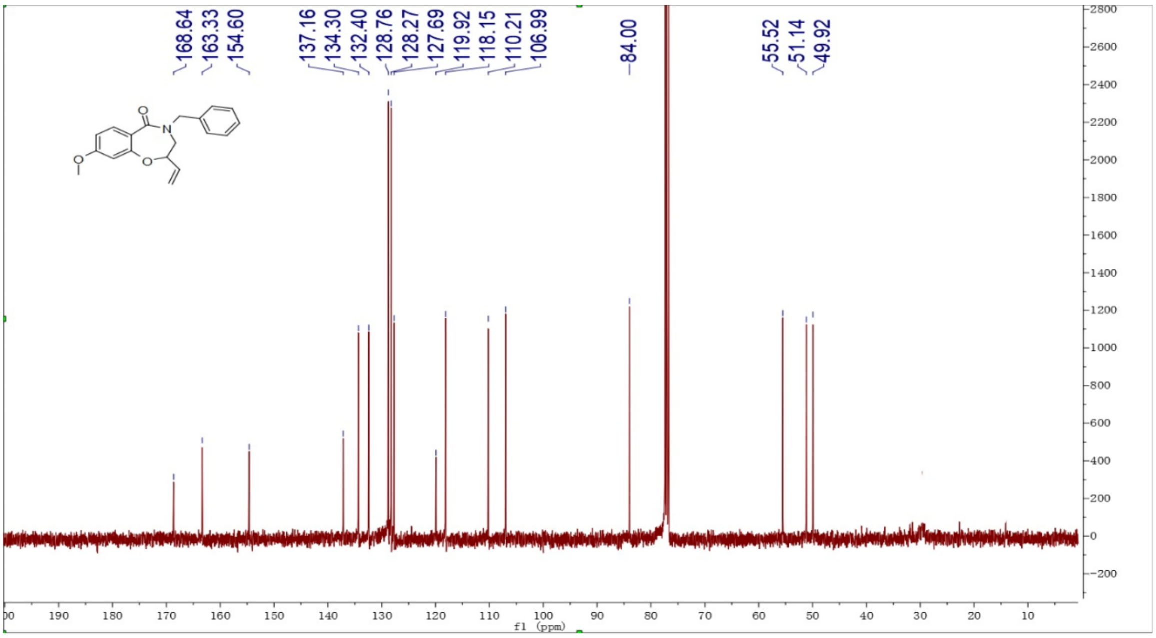


Figure 61. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2f



4-Benzyl-7-methoxy-2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (2g)

Figure 62. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2g

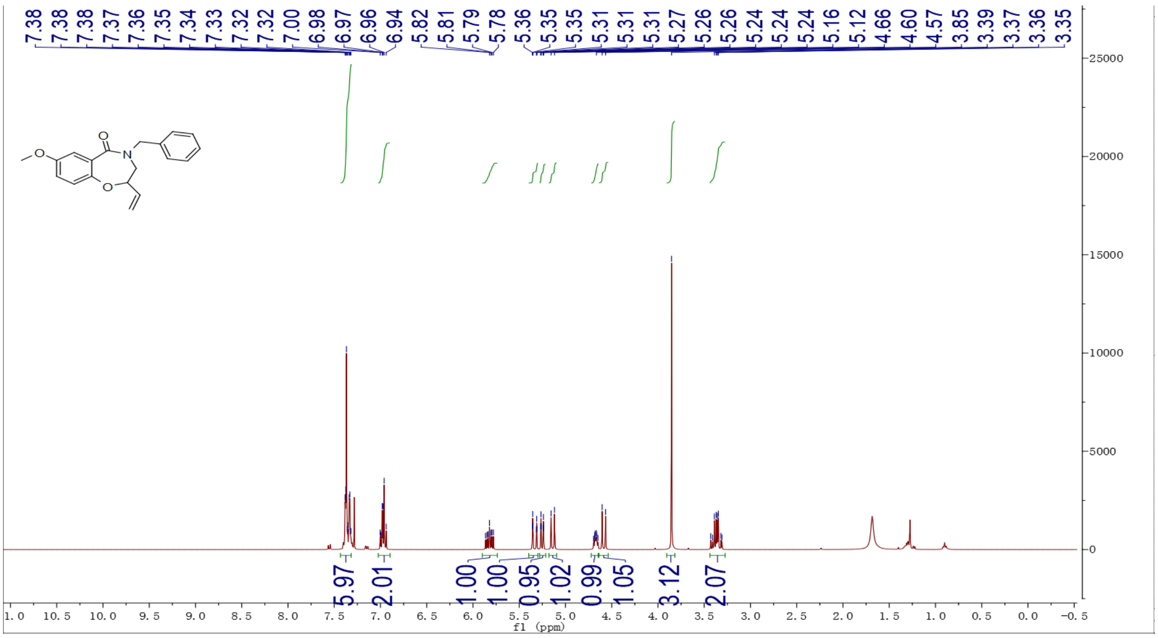
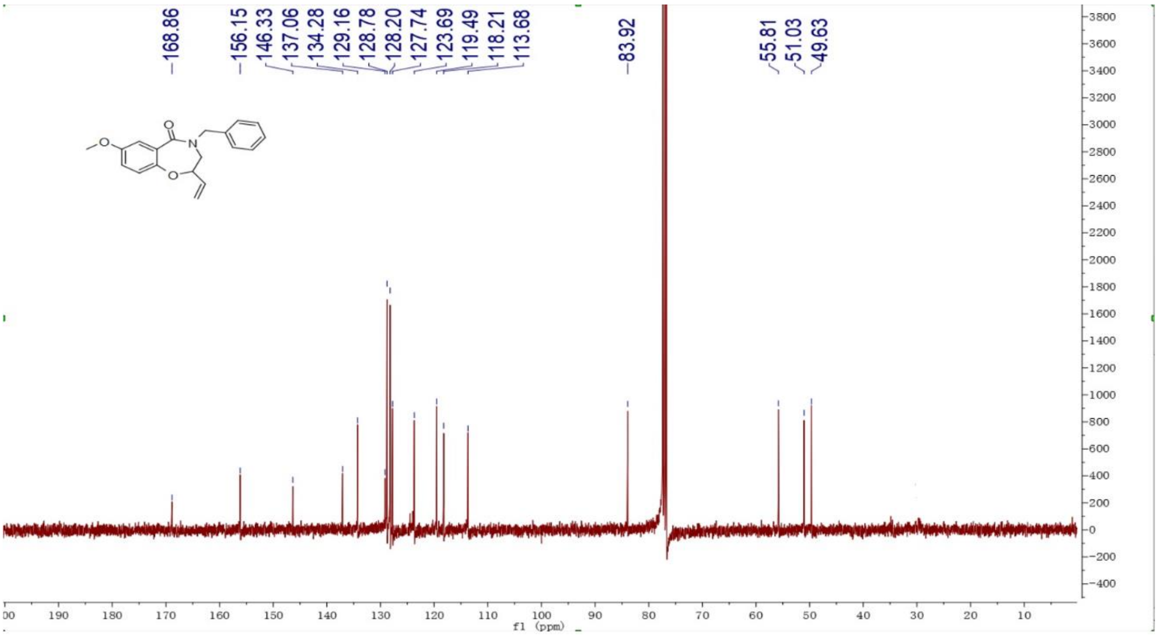


Figure 63. ^{13}C **NMR (100 MHz, CDCl$_3$) spectrum of 2g**



4-Benzyl-6-methoxy-2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (2h)

Figure 64. ^{1}H **NMR (400 MHz, CDCl$_3$) spectrum of 2h**

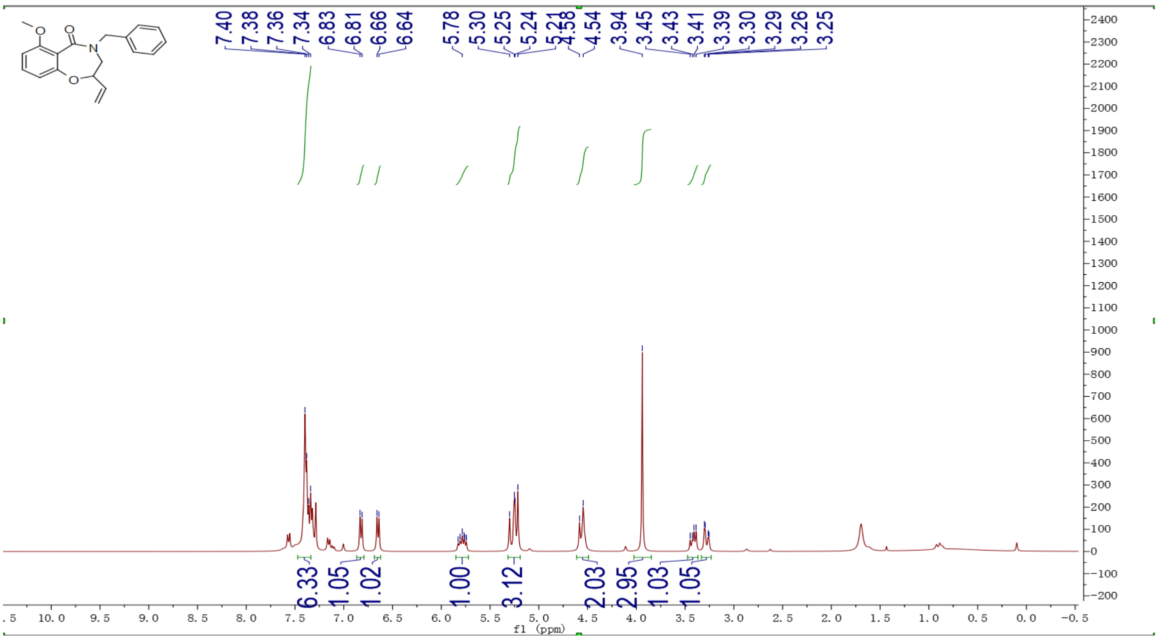
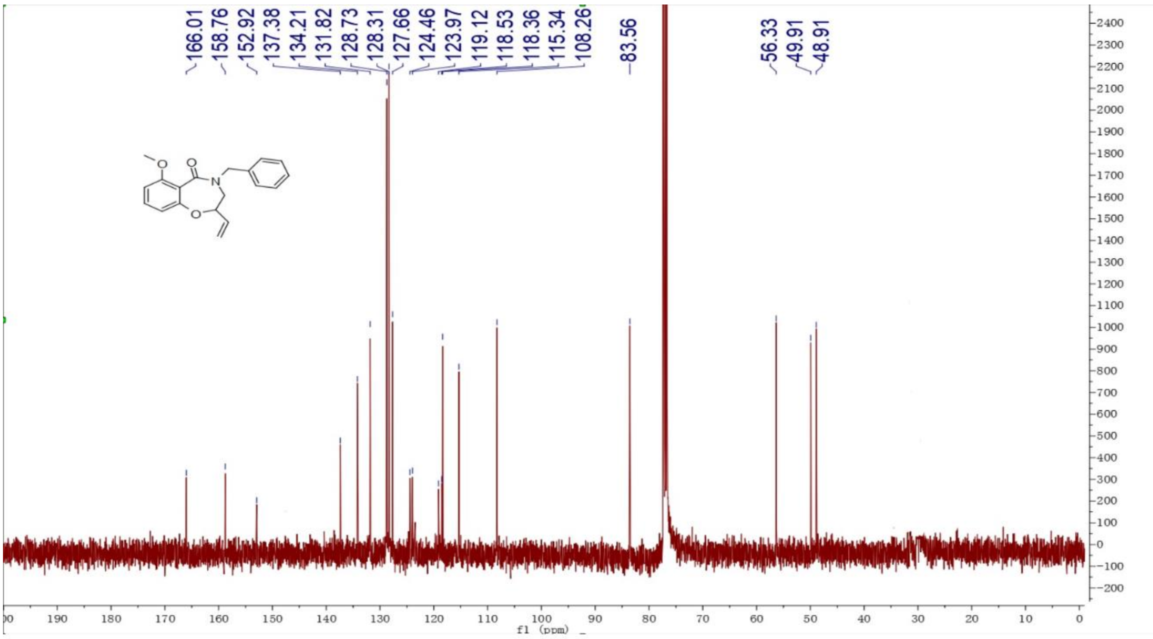


Figure 65. ^{13}**C NMR (100 MHz, CDCl$_3$) spectrum of 2h**



4-Benzyl-8-fluoro-2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (2i)

Figure 66. ^{1}**H NMR (400 MHz, CDCl$_3$) spectrum of 2i**

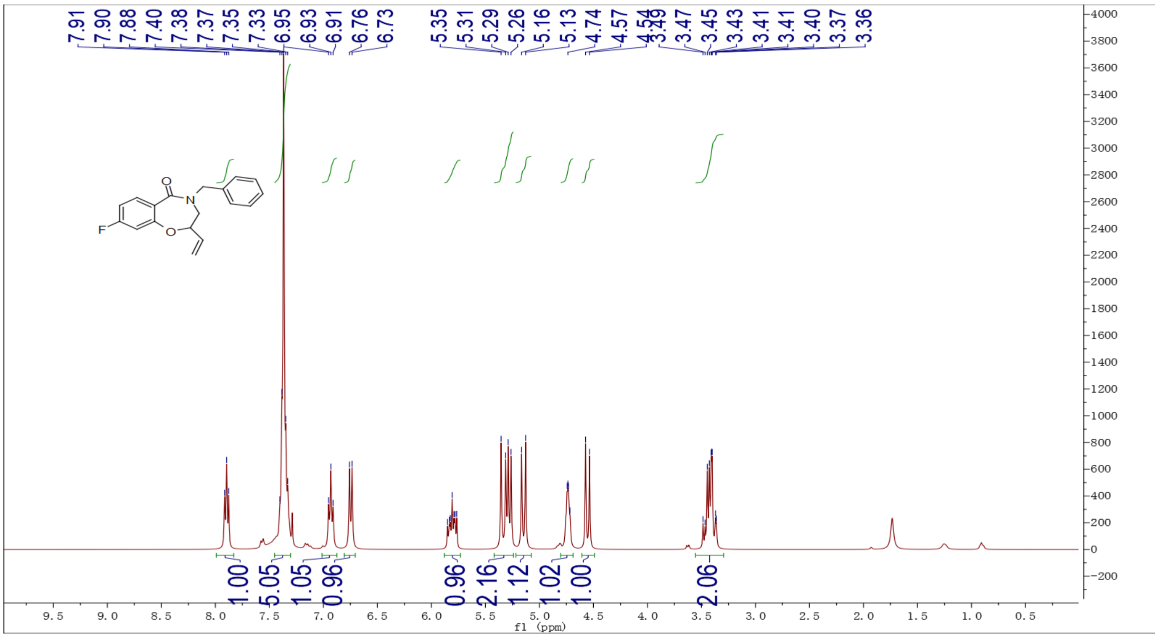


Figure 67. ^{13}**C NMR (100 MHz, CDCl$_3$) spectrum of 2i**

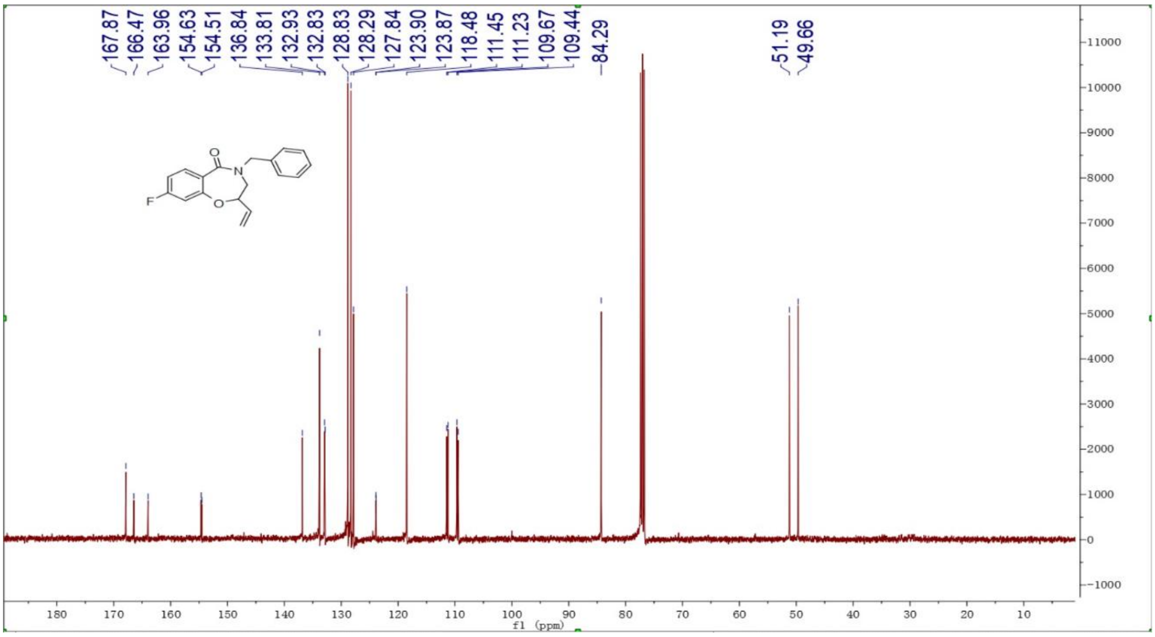
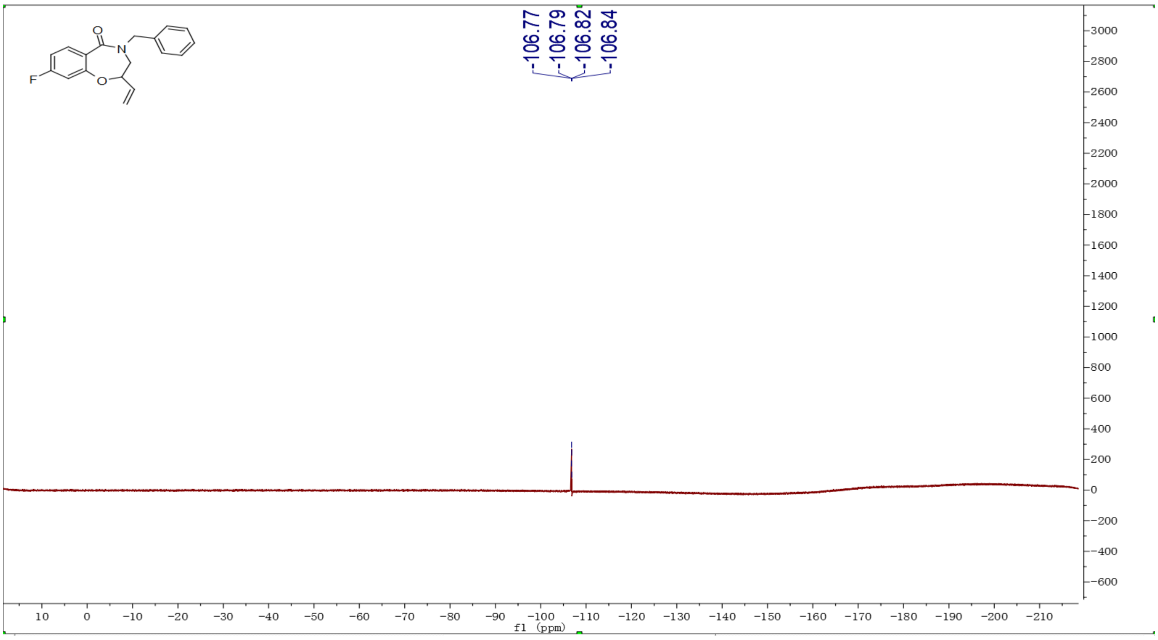


Figure 68. ^{19}**F NMR (376 MHz, CDCl$_3$) spectrum of 2i**



4-Benzyl-7-fluoro-2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (2j)

Figure 69. [1]H NMR (400 MHz, $CDCl_3$) spectrum of 2j

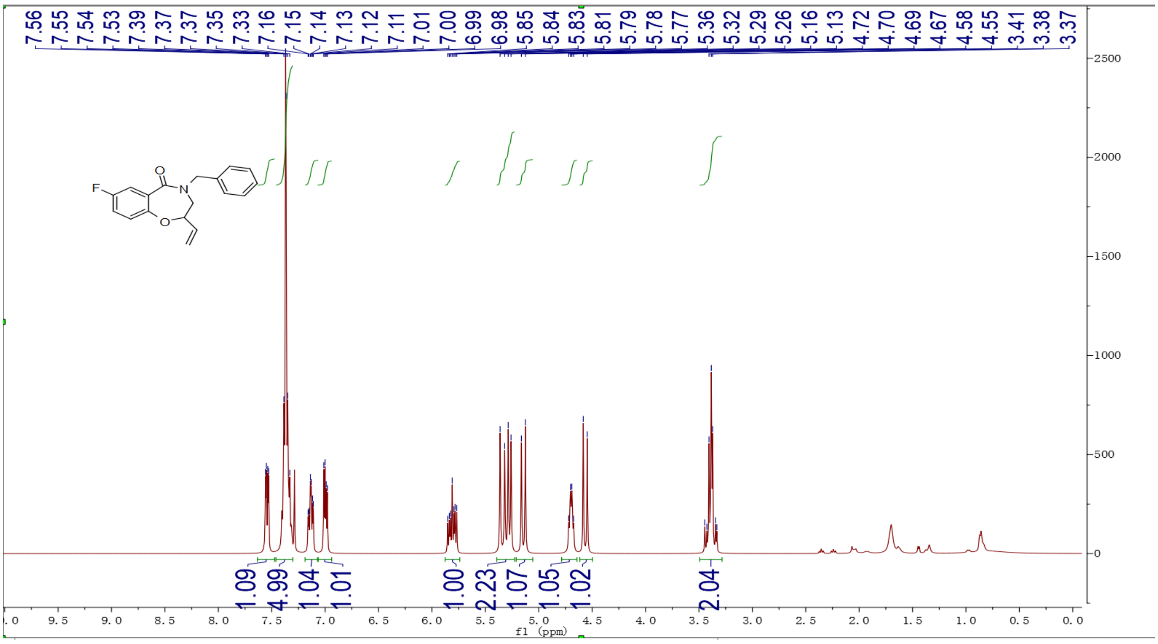


Figure 70. [13]C NMR (100 MHz, $CDCl_3$) spectrum of 2j

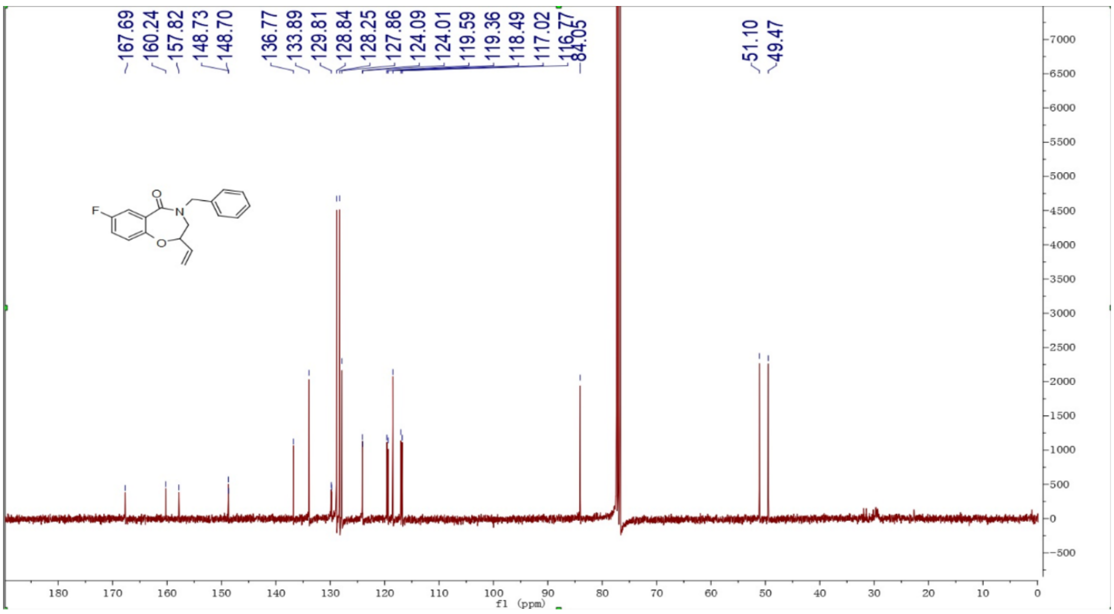
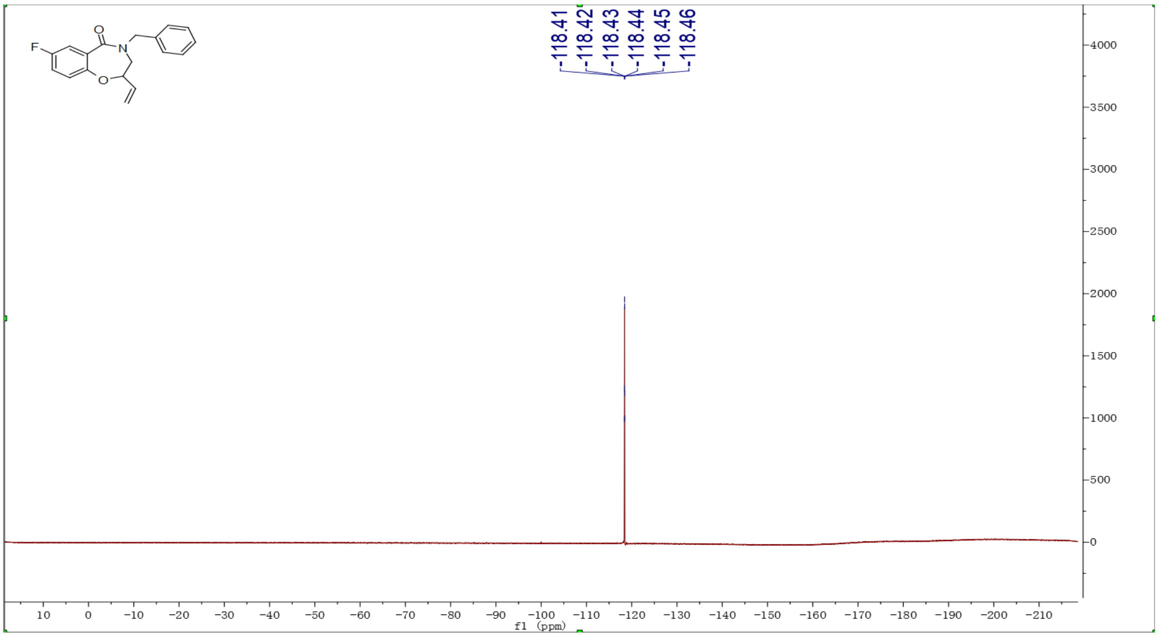


Figure 71. ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 2j



4-Benzyl-8-chloro-2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (2k)

Figure 72. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2k

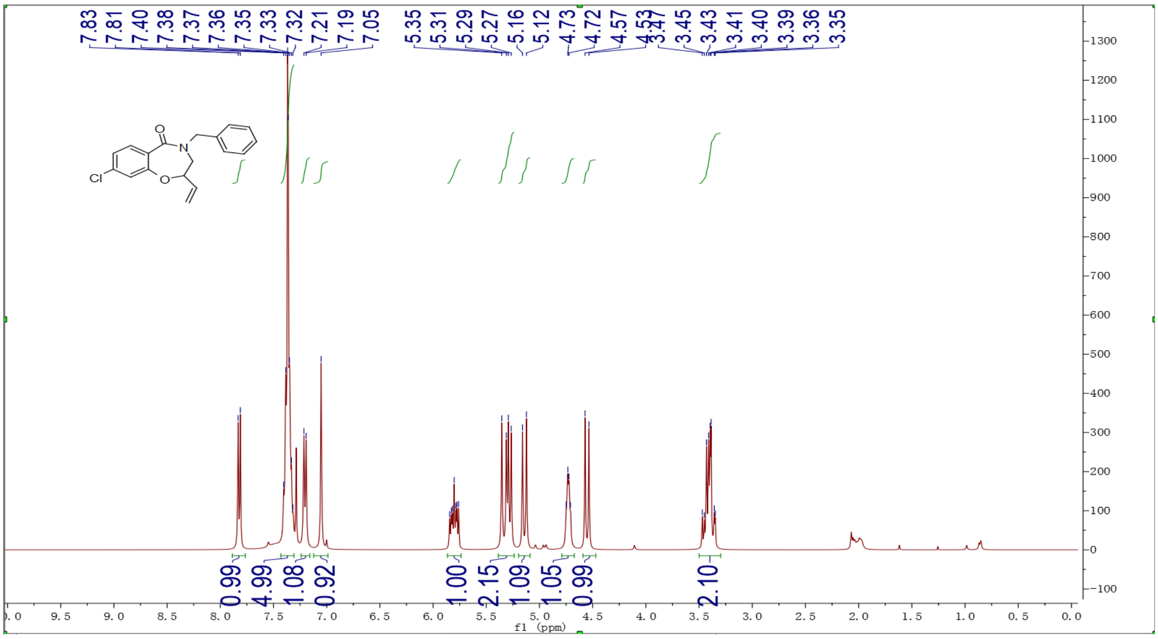
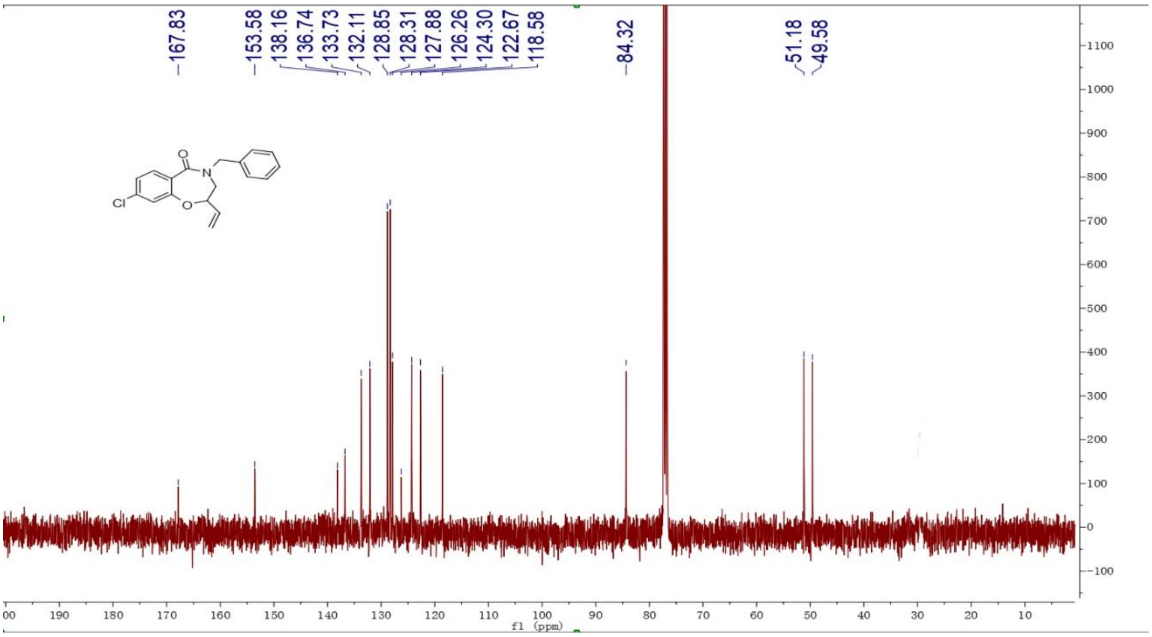


Figure 73. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2k



4-Benzyl-7-chloro-2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (2l)

Figure 74. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2l

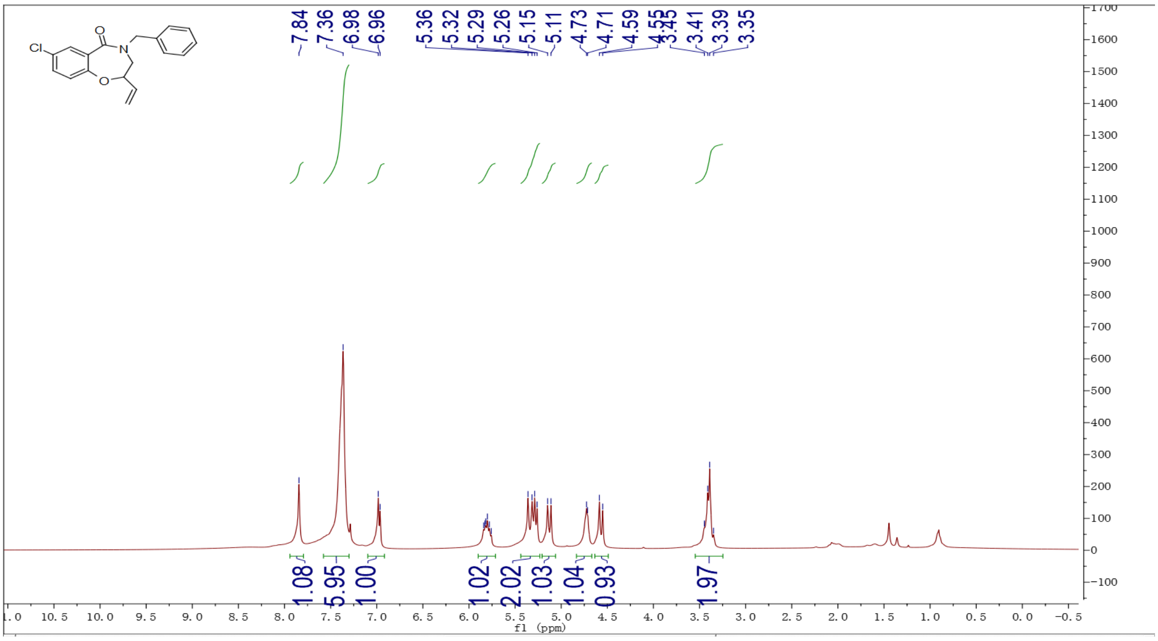
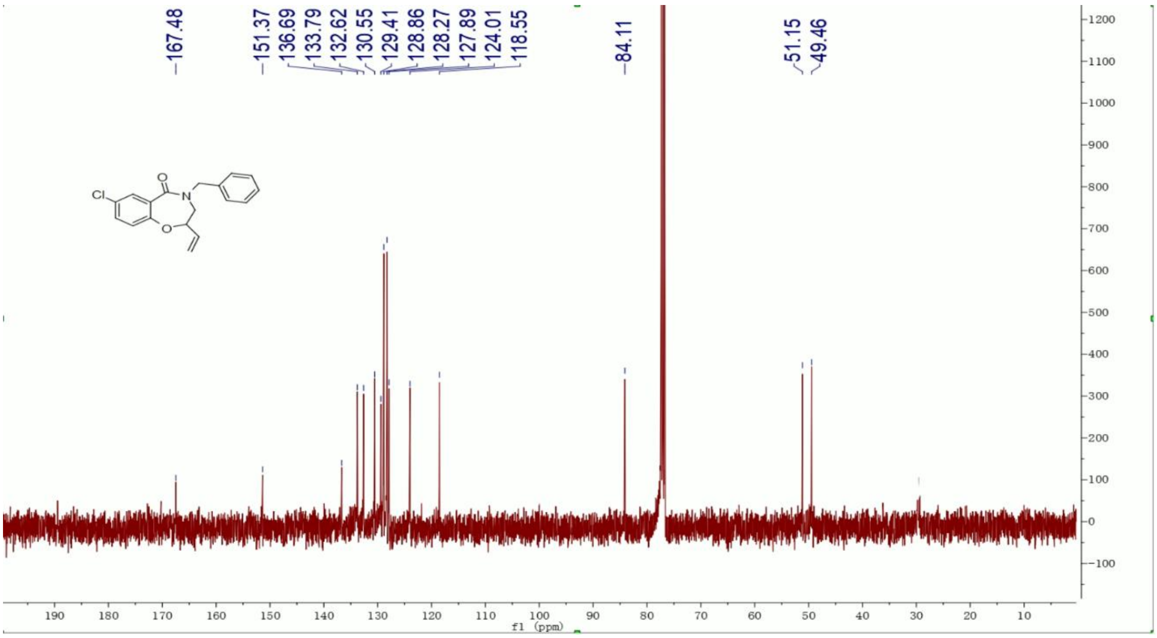


Figure 75. ^{13}C **NMR (100 MHz,** $CDCl_3$**) spectrum of 2l**



4-Benzyl-7-bromo-2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (2m)

Figure 76. ^{1}H **NMR (400 MHz,** $CDCl_3$**) spectrum of 2m**

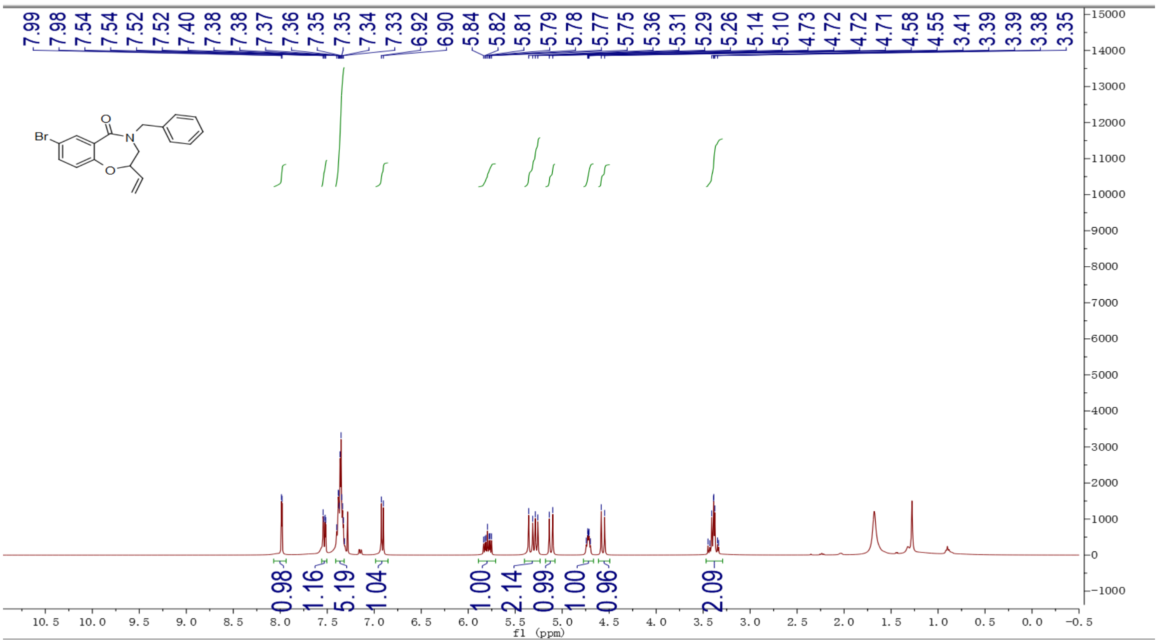
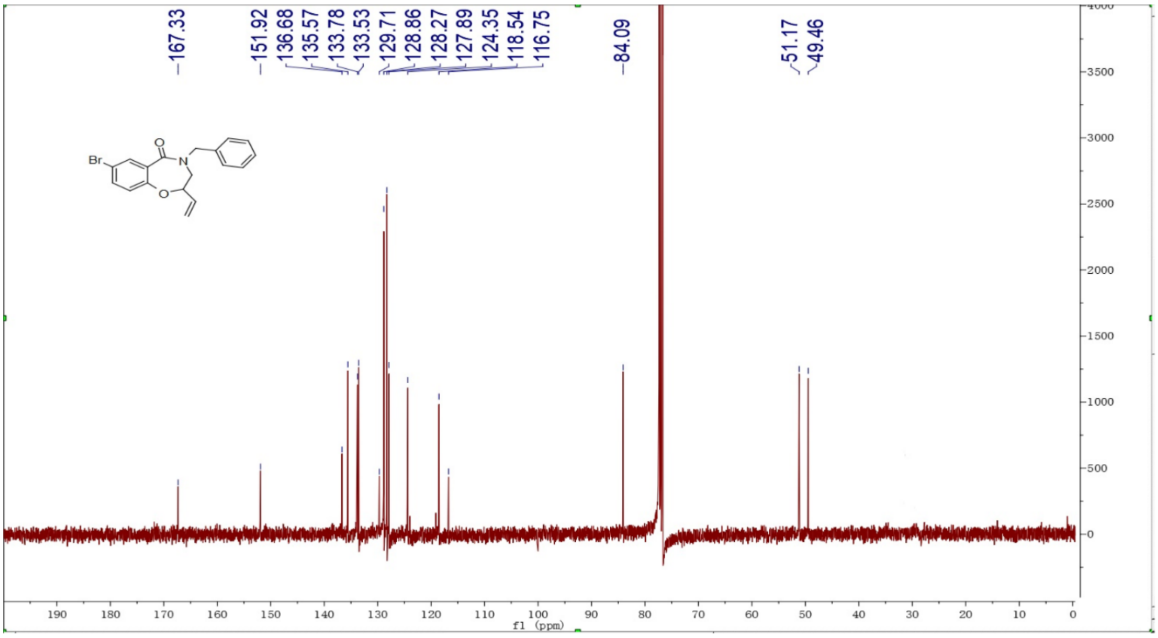


Figure 77. ^{13}**C NMR (100 MHz, CDCl$_3$) spectrum of 2m**



4-Benzyl-8-nitro-2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (2n)

Figure 78. ^{1}**H NMR (400 MHz, CDCl$_3$) spectrum of 2n**

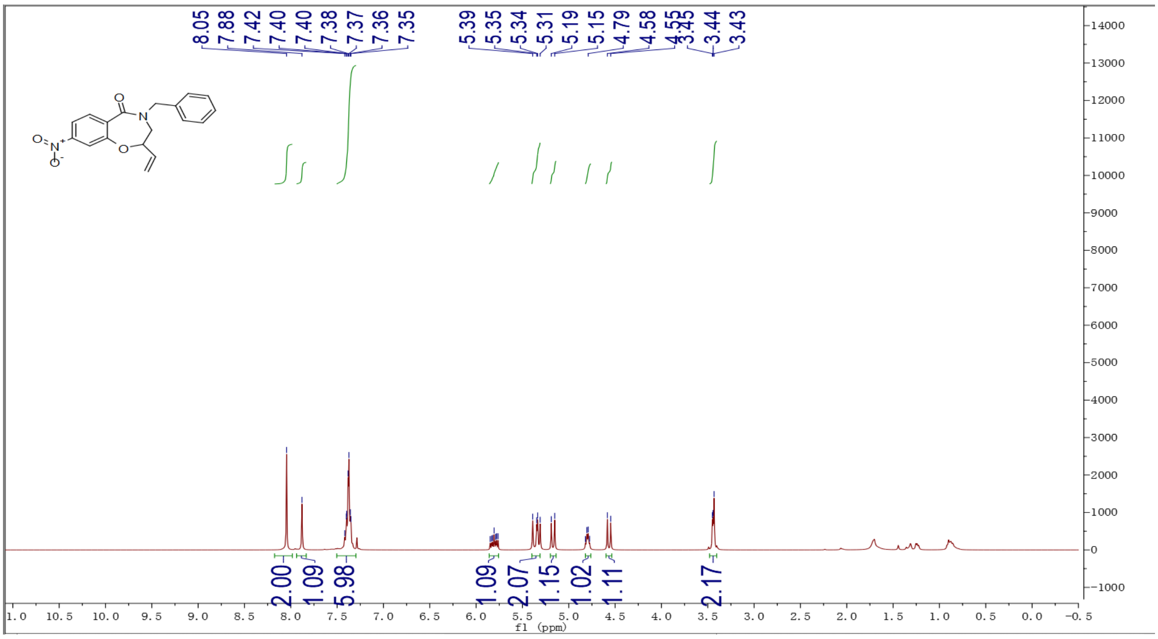
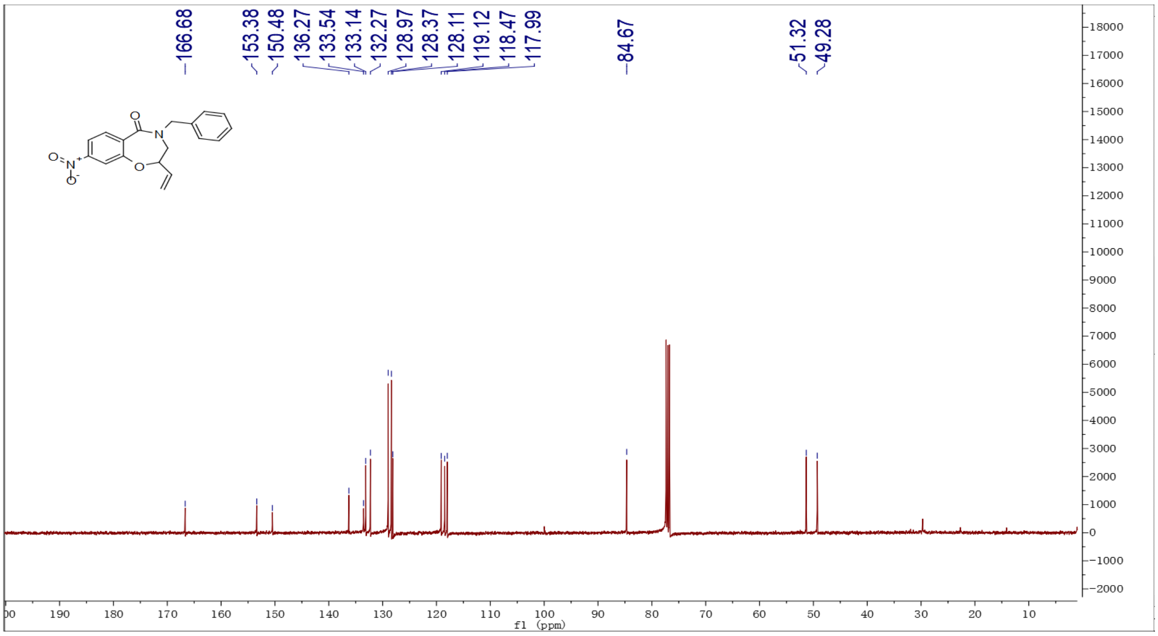


Figure 79. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2n



4-Benzyl-8-(trifluoromethyl)-2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (2o)

Figure 80. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2o

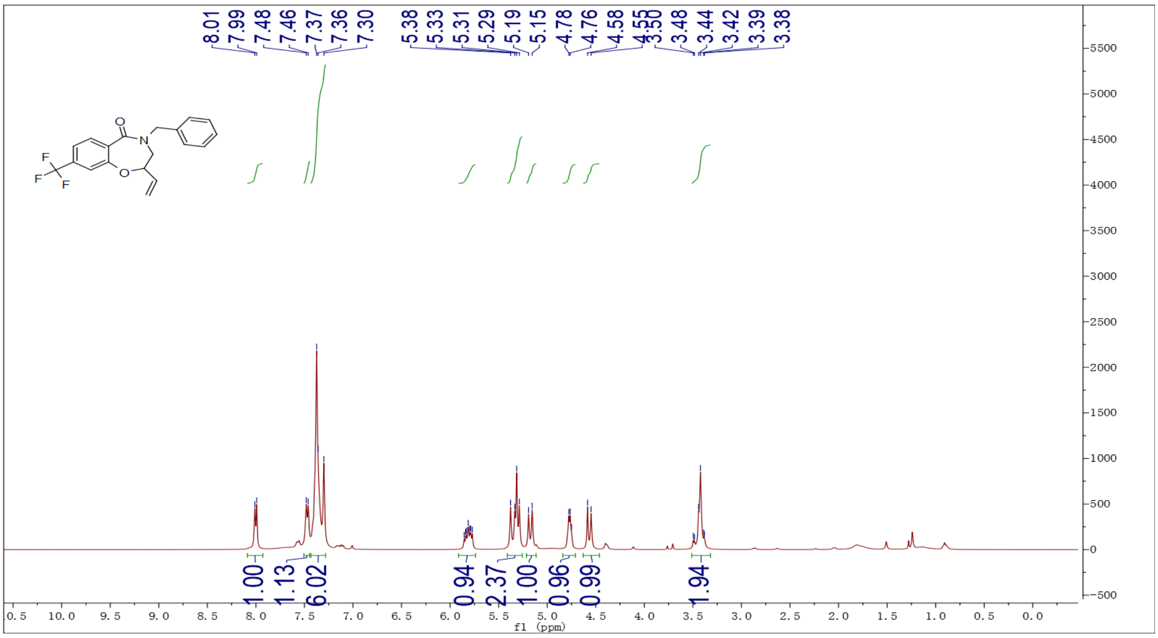


Figure 81. ^{13}**C NMR (100 MHz, CDCl**$_3$**) spectrum of 2o**

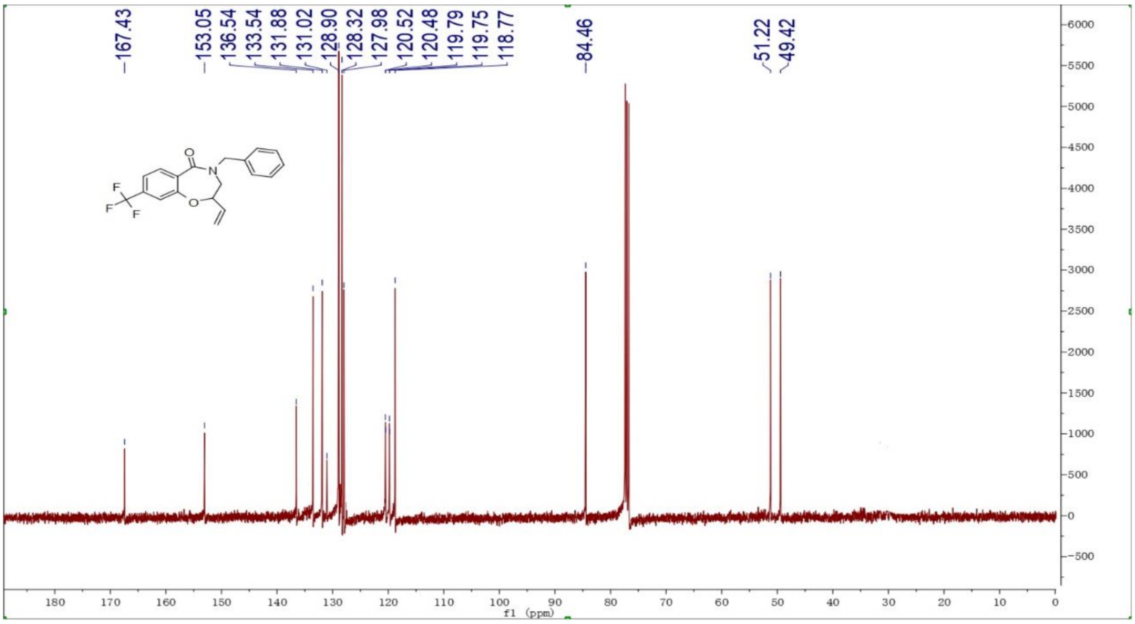
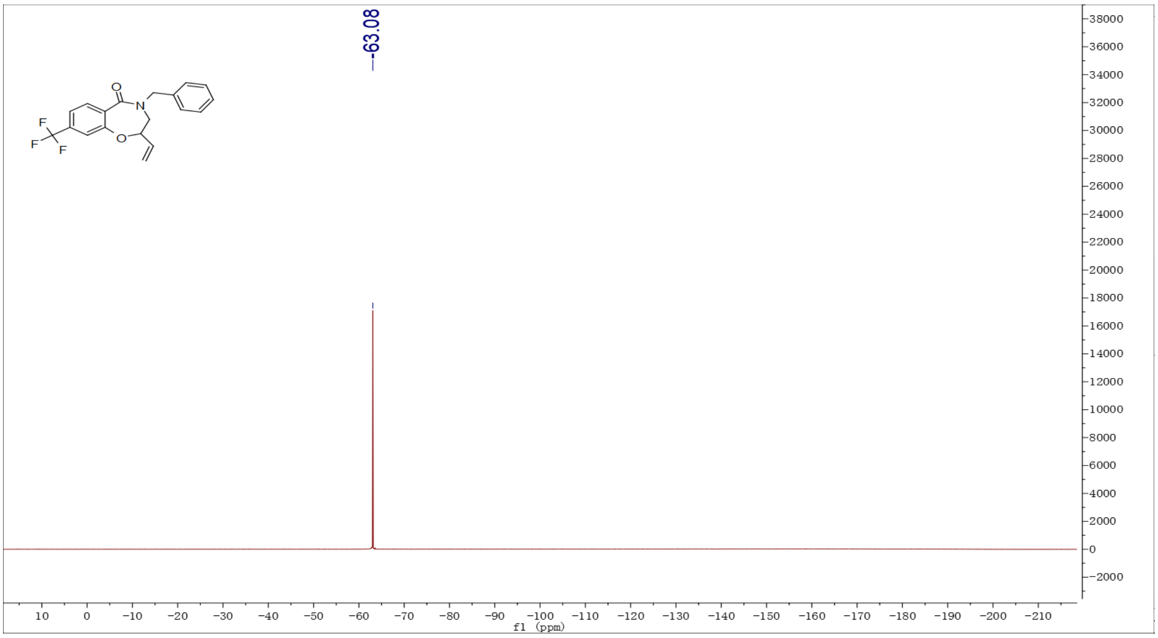


Figure 82. ^{19}**F NMR (376 MHz, CDCl**$_3$**) spectrum of 2o**



4-Benzyl-2-vinyl-3,4-dihydronaphtho[2,3-*f*][1,4]oxazepin-5(2*H*)-one (2p)

Figure 83. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of 2p

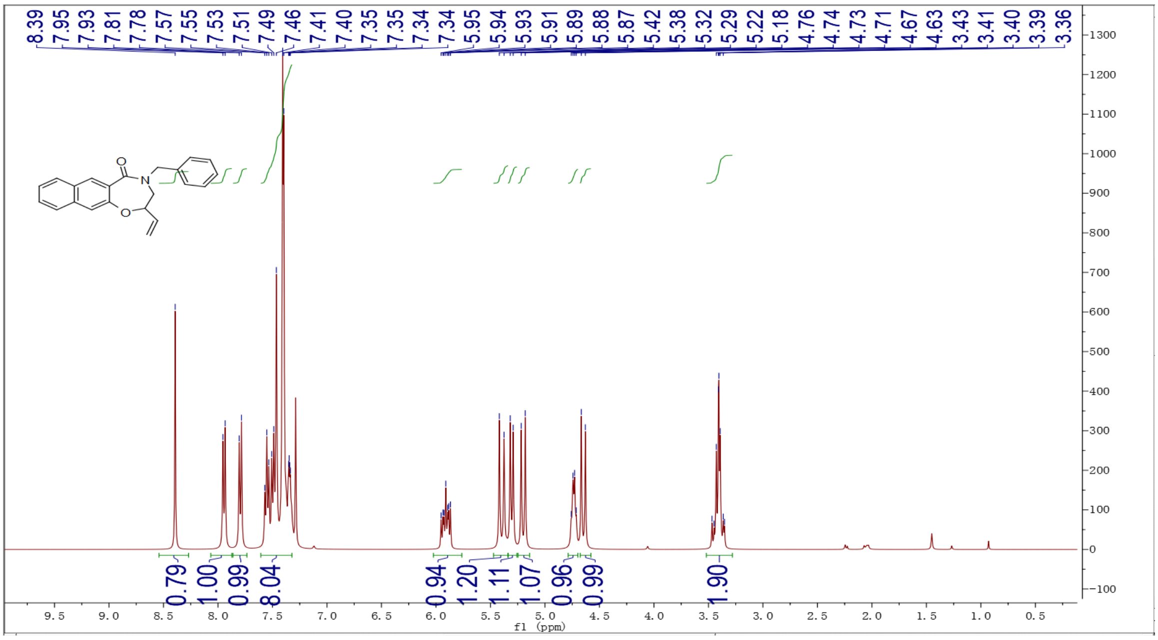
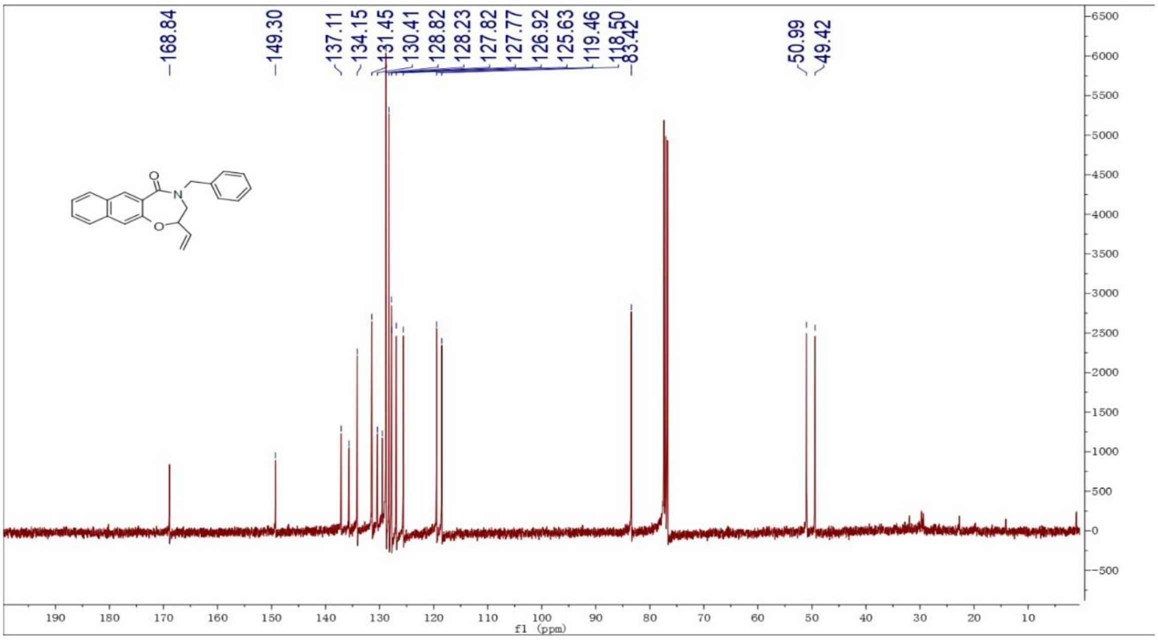


Figure 84. ^{13}C NMR (100 MHz, CDCl$_3$) spectrum of 2p



4-Benzyl-2-vinyl-3,4-dihydropyrido[4,3-*f*][1,4]oxazepin-5(2*H*)-one (2q)

Figure 85. ^{1}H **NMR (400 MHz,** $CDCl_3$**) spectrum of 2q**

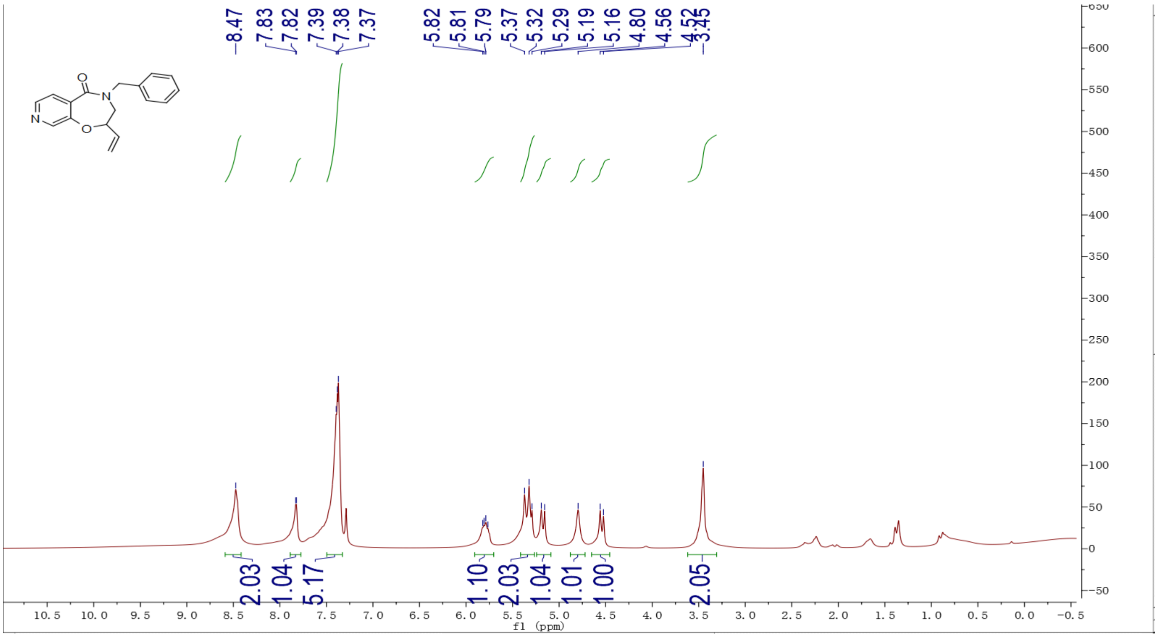
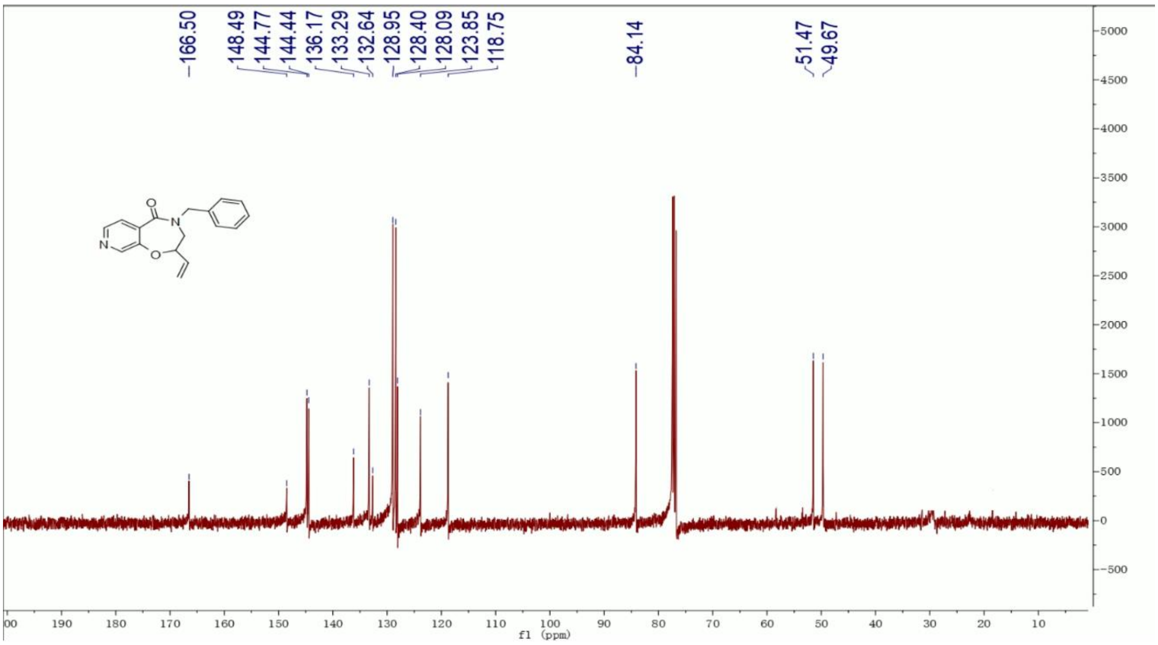


Figure 86. ^{13}C **NMR (100 MHz,** $CDCl_3$**) spectrum of 2q**



4-Benzyl-8-(thiophen-3-yl)-2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (2r)

Figure 87. [1]H NMR (400 MHz, $CDCl_3$) spectrum of 2r

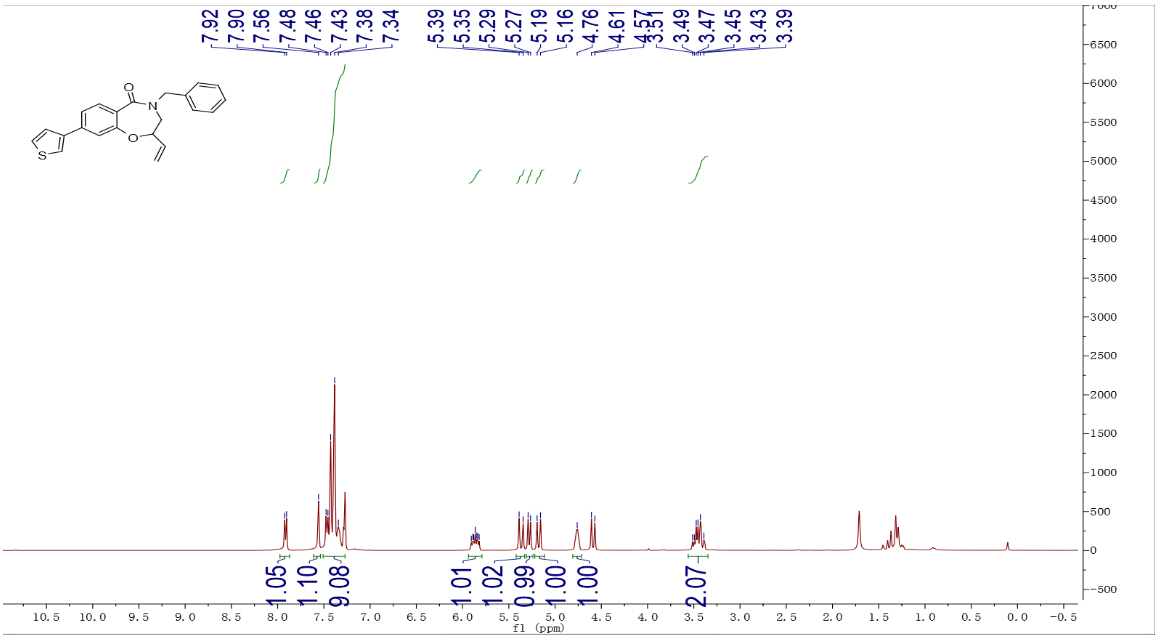
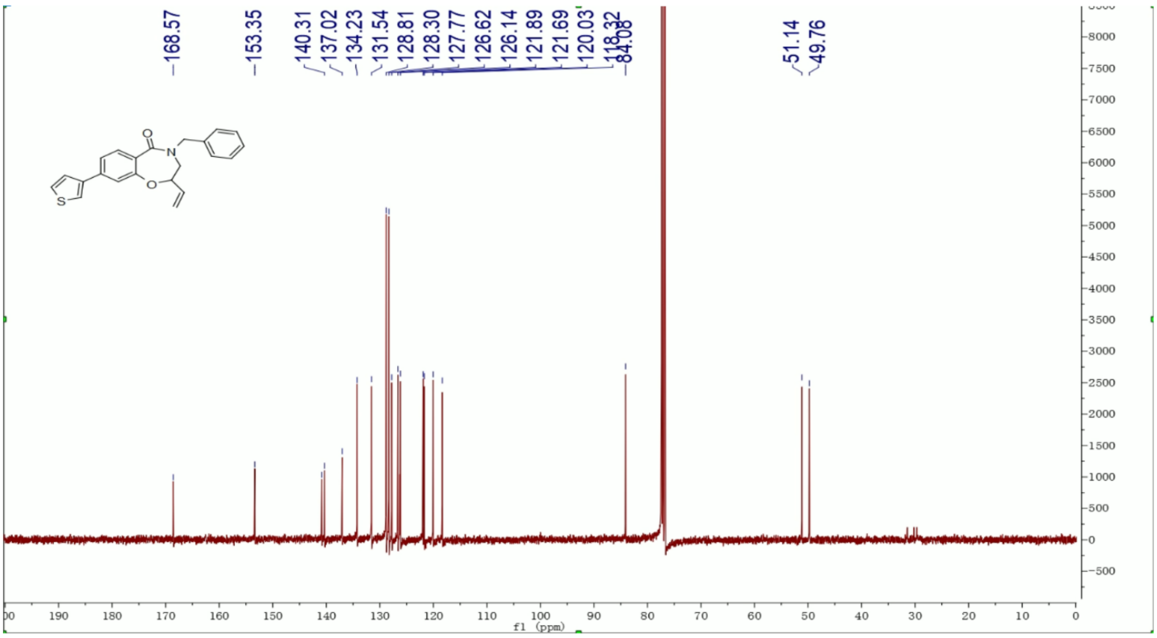


Figure 88. [13]C NMR (100 MHz, $CDCl_3$) spectrum of 2r



4-Benzyl-8-(furan-2-yl)-2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (2s)

Figure 89. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2s

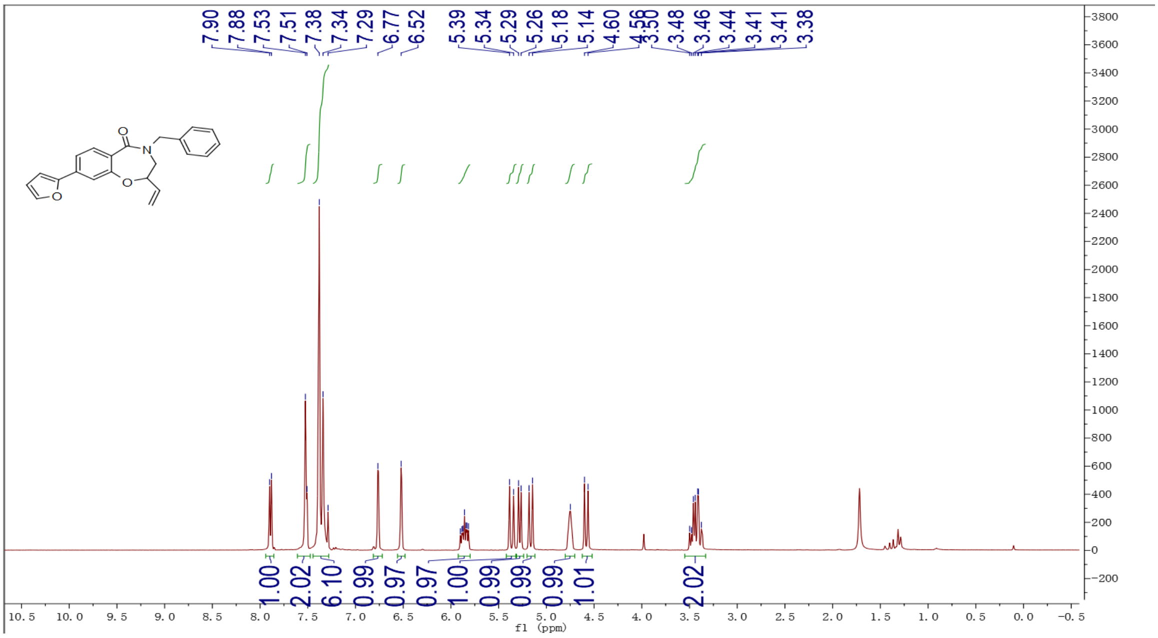
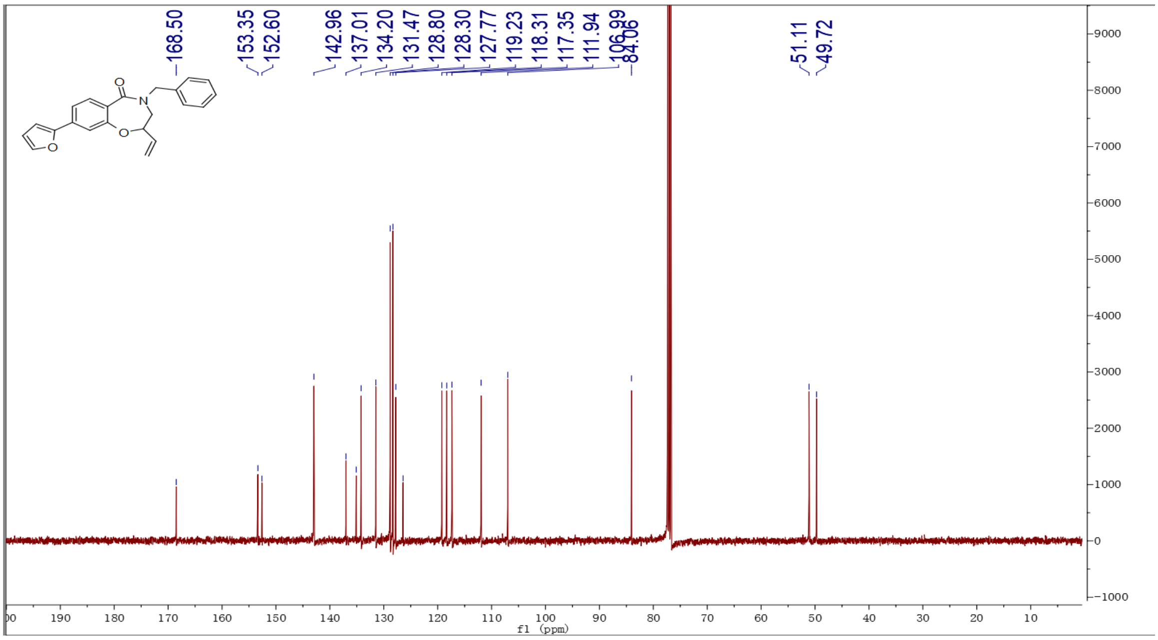


Figure 90. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2s



4-Benzyl-8-(6-methoxypyridin-3-yl)-2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (2t)

Figure 91. ^{1}**H NMR (400 MHz, CDCl$_3$) spectrum of 2t**

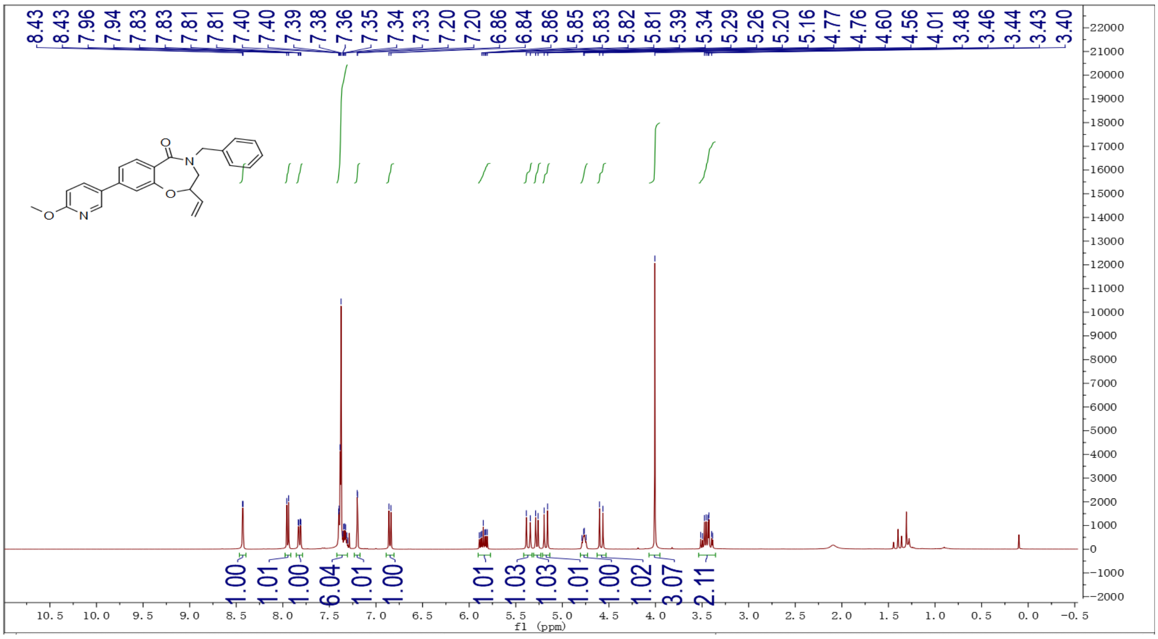
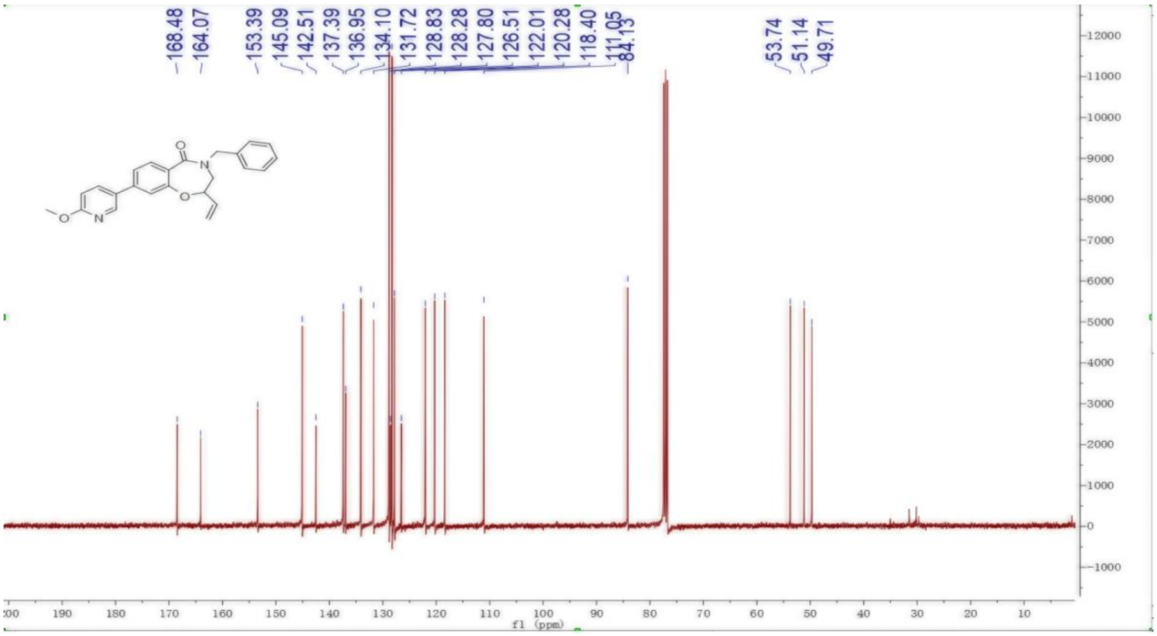


Figure 92. ^{13}**C NMR (100 MHz, CDCl$_3$) spectrum of 2t**



4-Benzyl-8-(naphthalen-2-yl)-2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (2u)

Figure 93. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2u

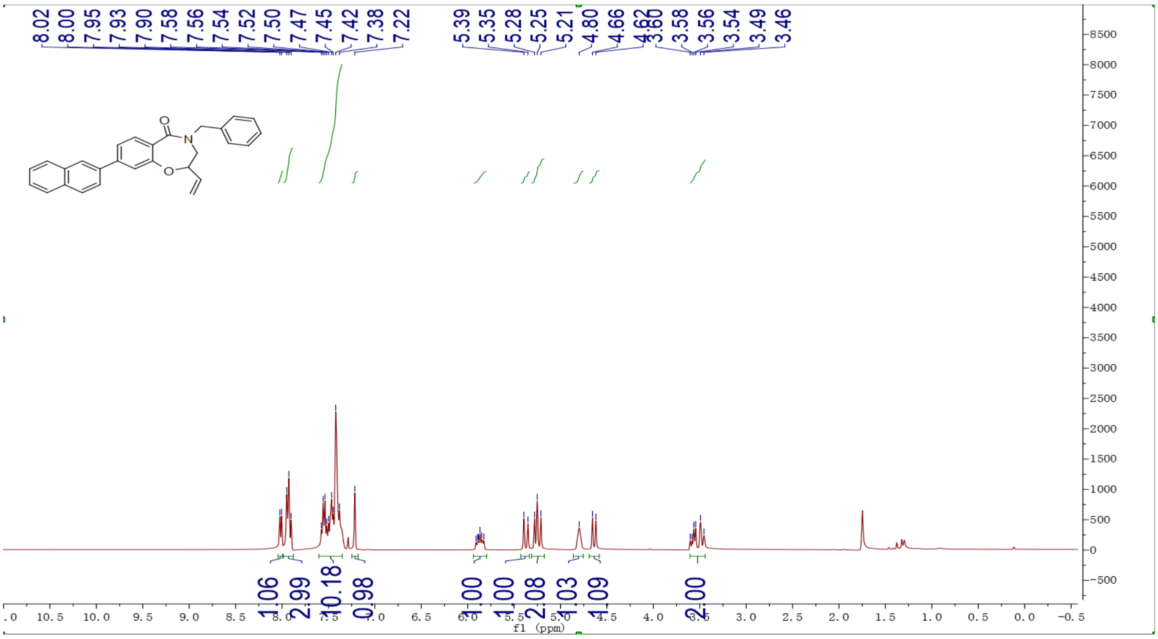
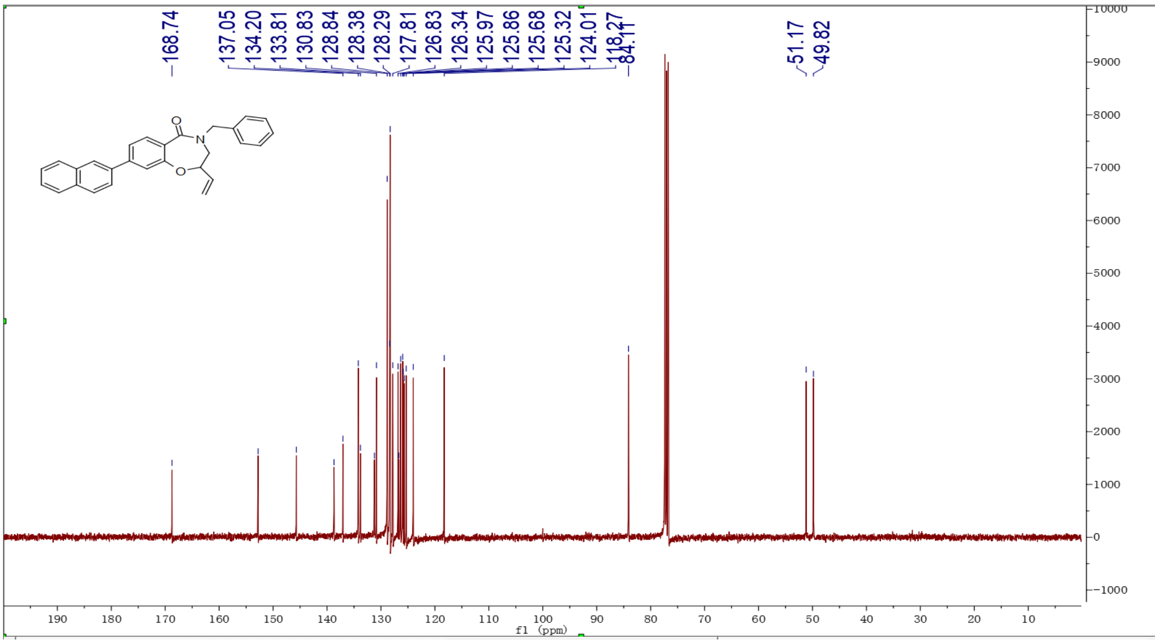


Figure 94. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2u



4-(4-Methoxybenzyl)-2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (2v)

Figure 95. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2v

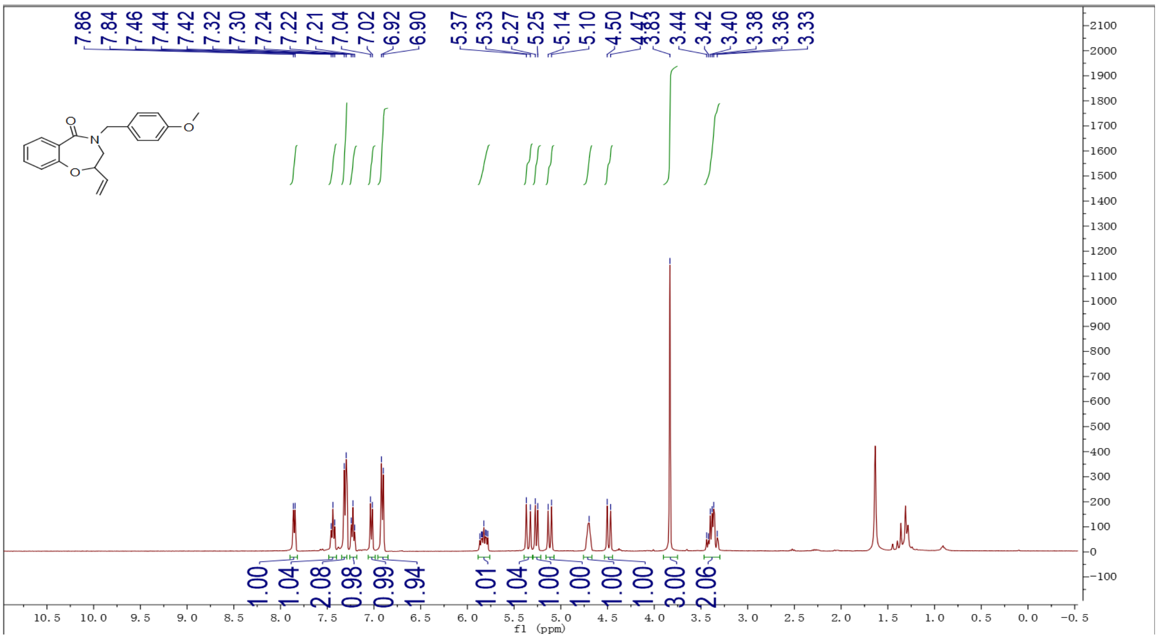
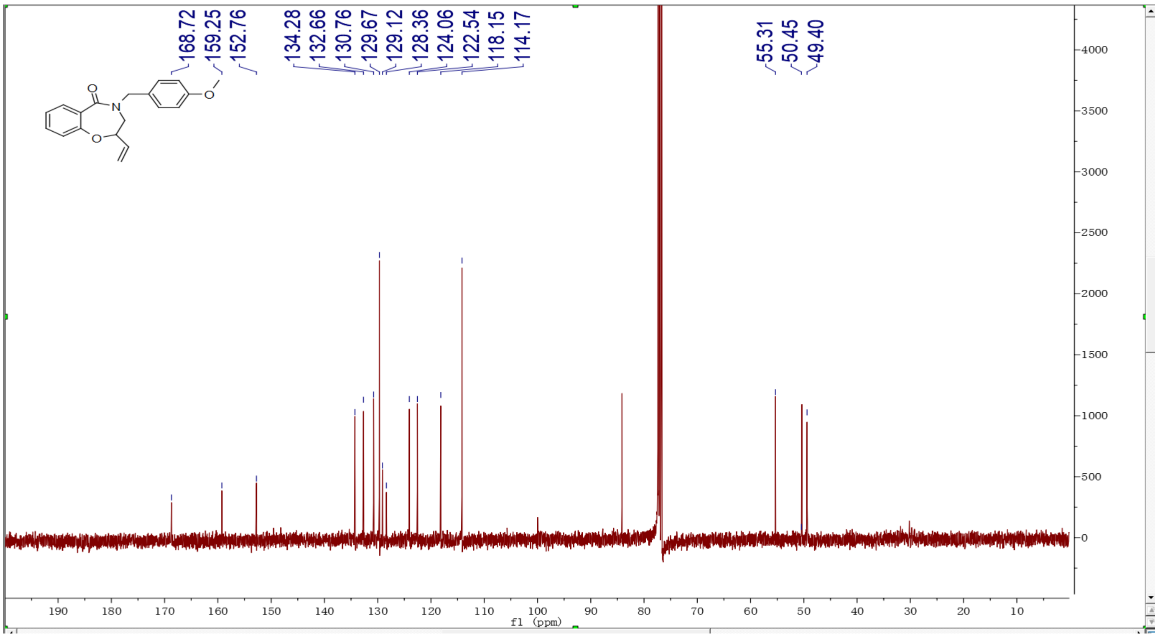


Figure 96. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2v



2-vinyl-3,4-dihydrobenzo[*f*][1,4]oxazepin-5(2*H*)-one (3v)

Figure 97. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3v

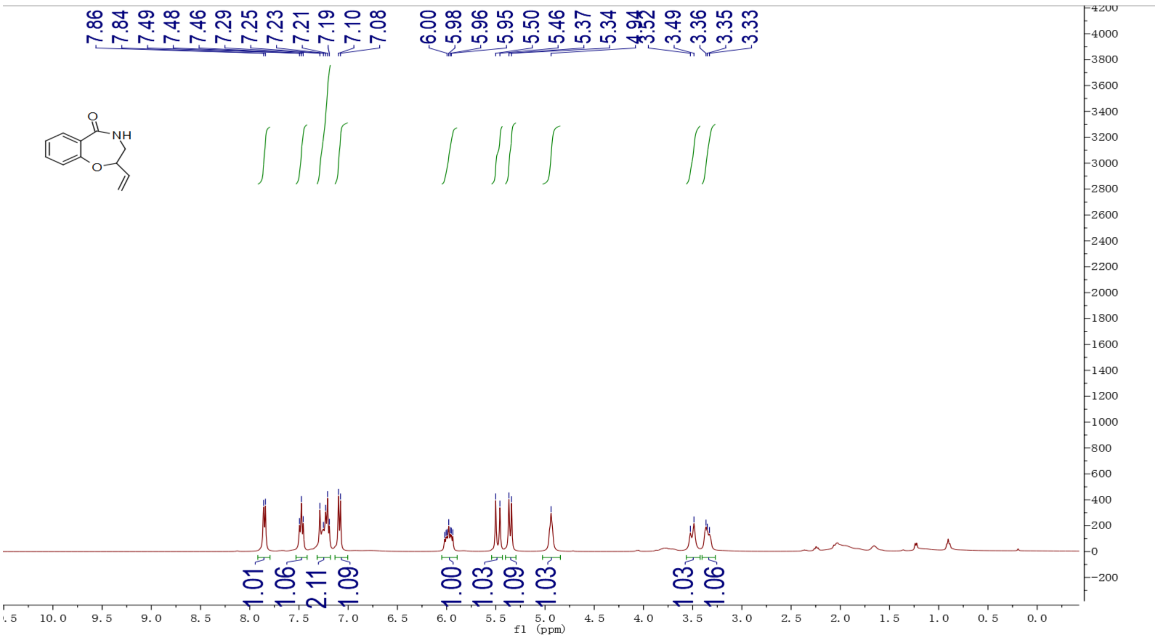
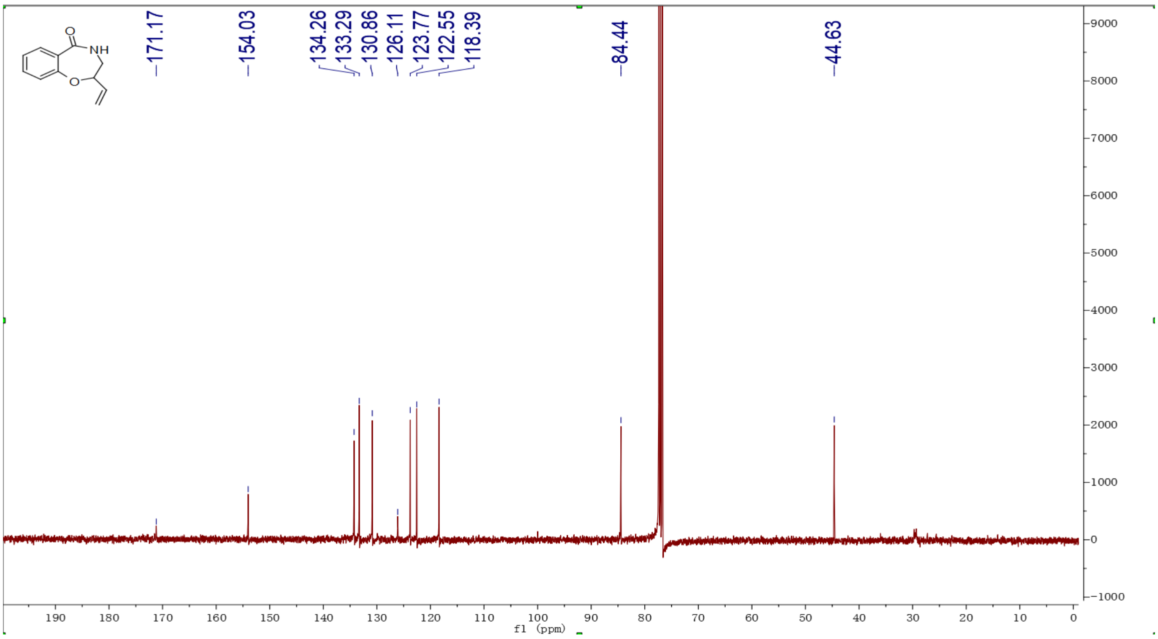


Figure 98. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3v



4-Benzyl-2-vinyl-2,3,4,5-tetrahydrobenzo[*f*][1,4]oxazepane (3a)

Figure 99. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3a

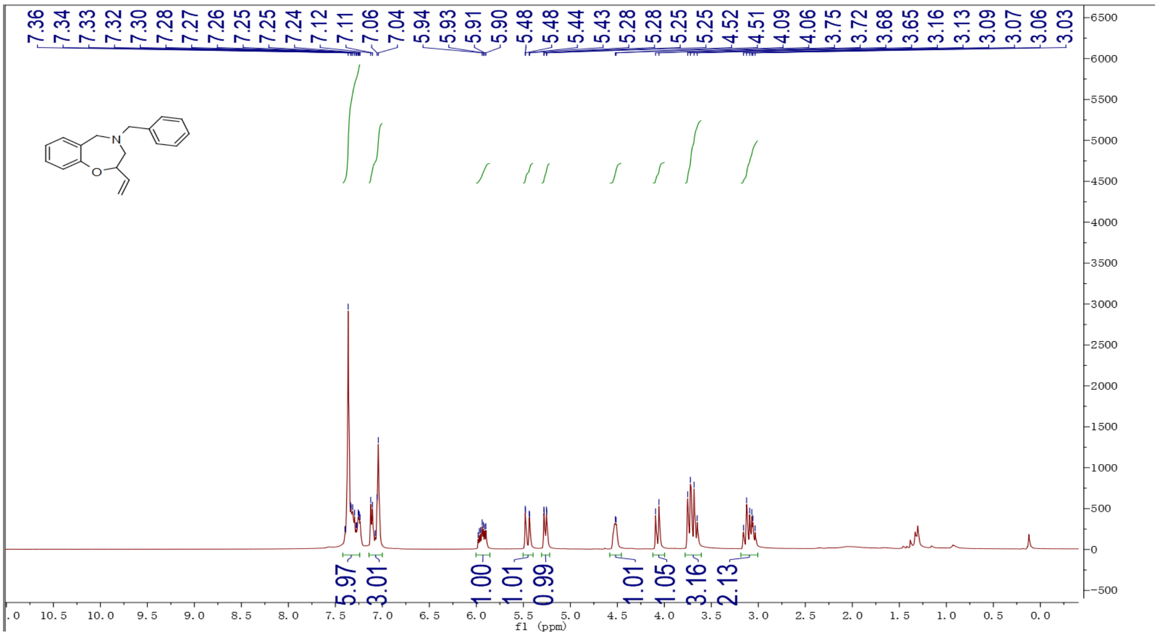
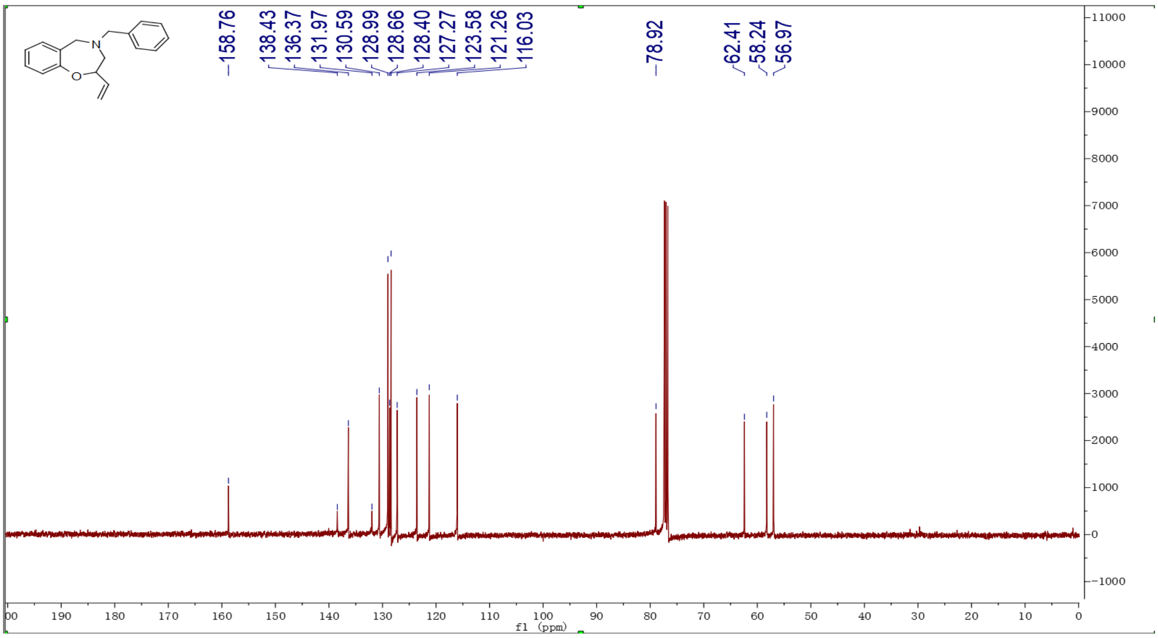


Figure 100. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3a



4-Benzyl-2-(2-hydroxyethyl)-3,4-dihydro-2λ[3]-benzo[*f*][1,4]oxazepin-5(2*H*)-one (4a)

Figure 101. ^{1}**H NMR (400 MHz,** $CDCl_3$**) spectrum of 4a**

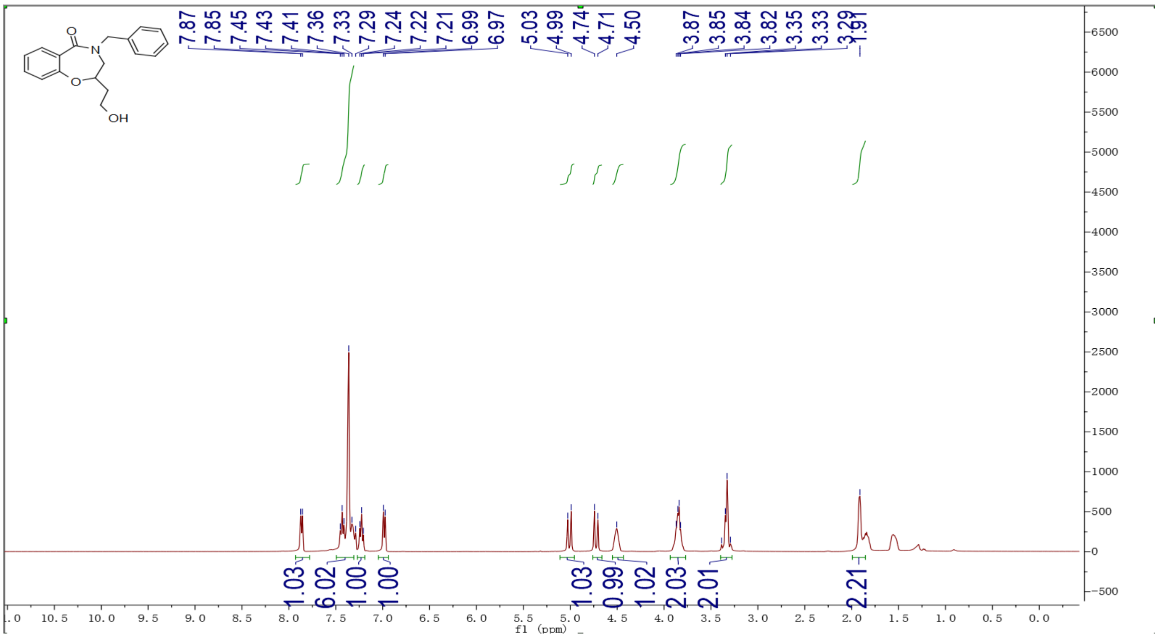
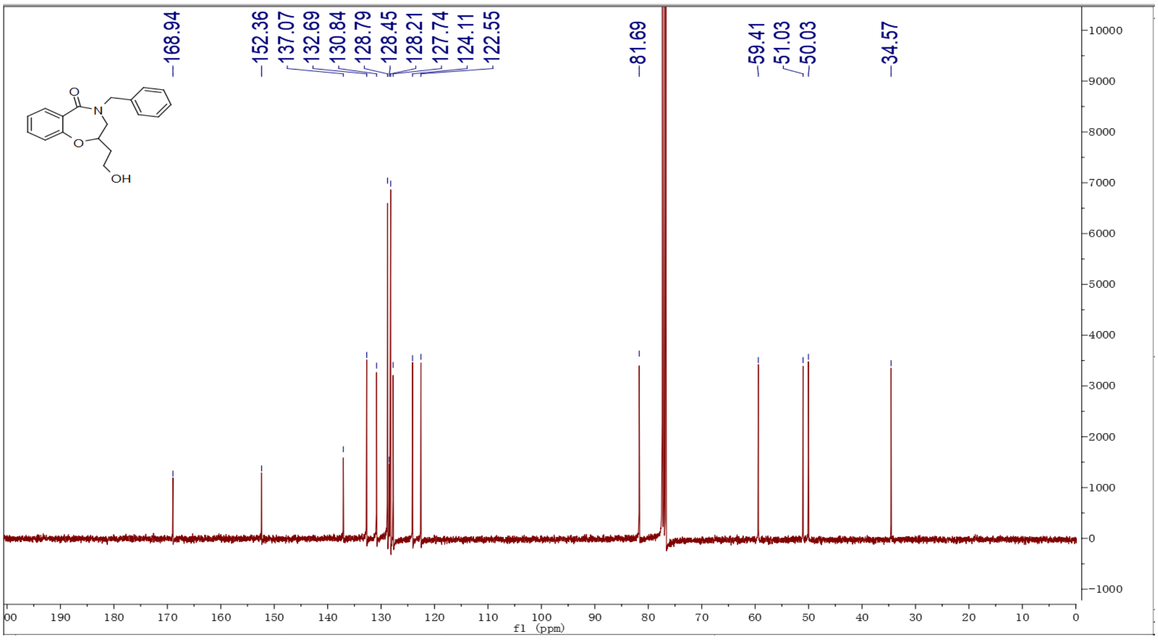
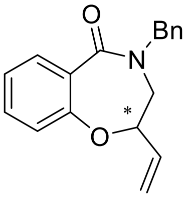


Figure 102. ^{13}**C NMR (100 MHz,** $CDCl_3$**) spectrum of 4a**

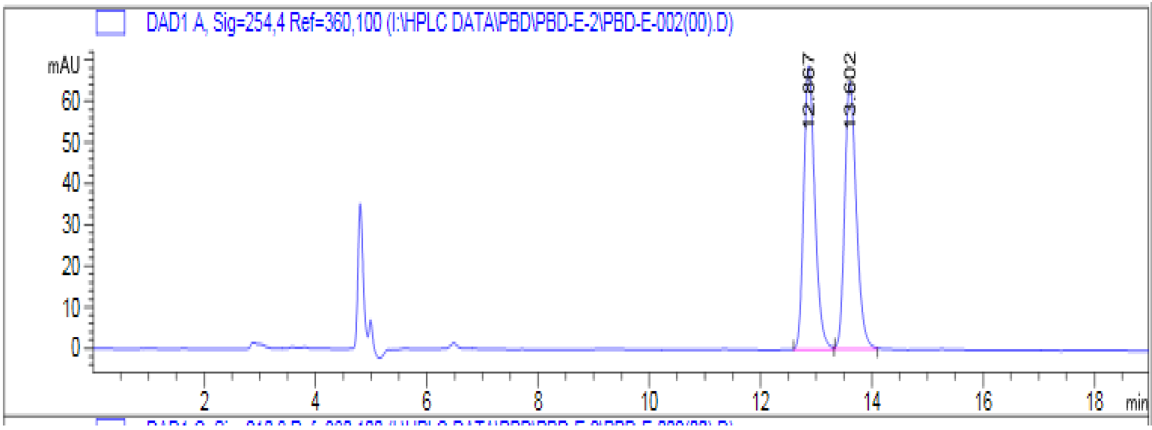


5. Copies of HPLC Chromatograms

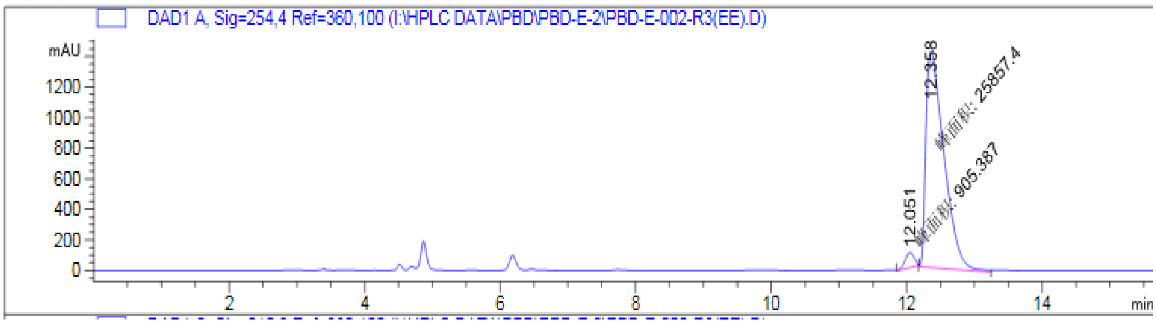
Figure 103. HPLC spectra of 2a



2a (The top one is racemic, and the bottom one is chiral)

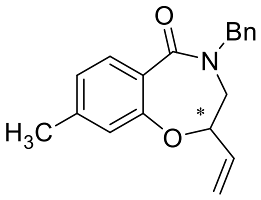


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	12.867	BB	0.2123	958.95203	68.94242	50.2563
2	13.602	BB	0.2240	949.17218	65.12415	49.7437

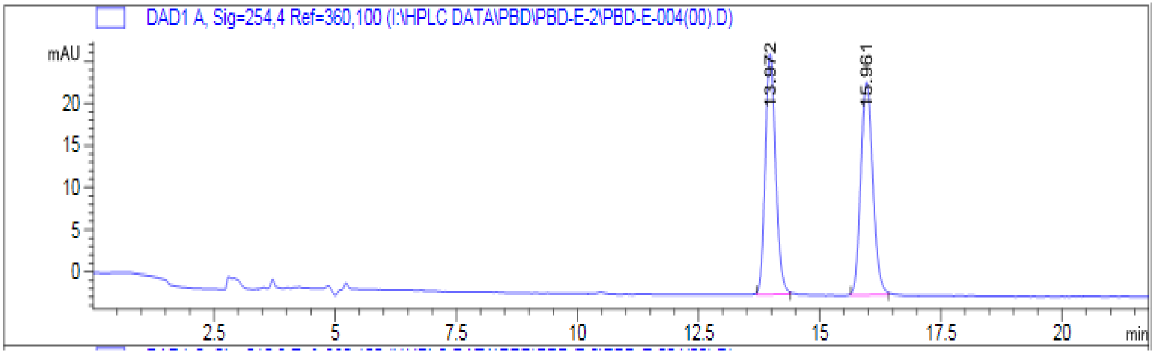


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	12.051	MM	0.1550	905.38708	97.36284	3.3830
2	12.358	MM	0.3035	2.58574e4	1419.93005	96.6170

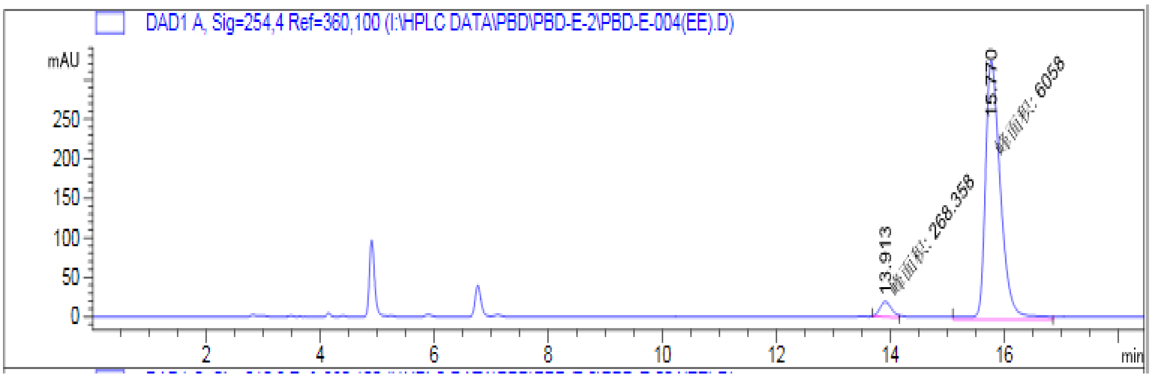
Figure 104. HPLC spectra of 2b



2b (The top one is racemic, and the bottom one is chiral)

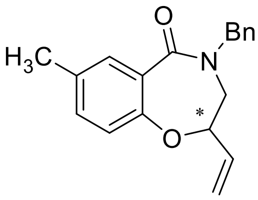


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	13.972	BB	0.2278	425.86673	28.59163	49.9355
2	15.961	BB	0.2611	426.96609	25.27287	50.0645

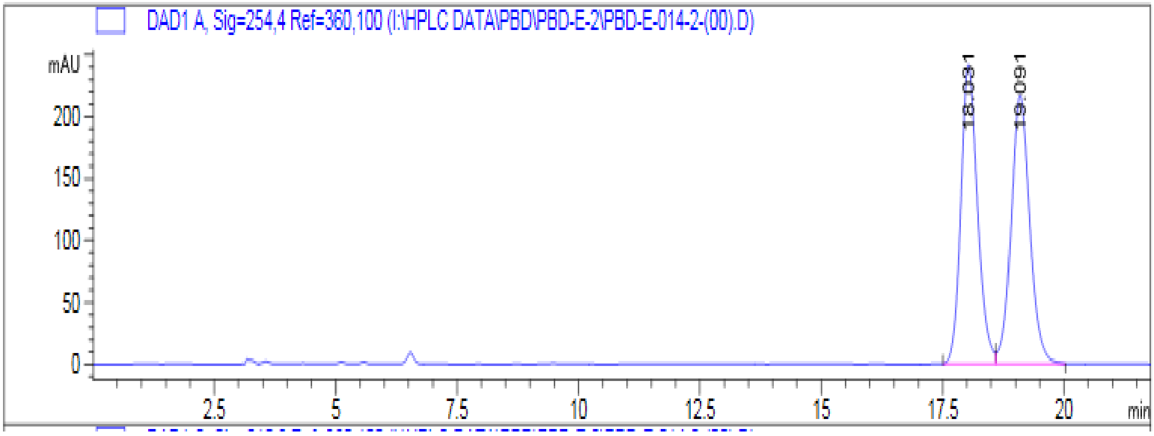


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	13.913	MM	0.2373	268.35806	18.84915	4.2419
2	15.770	MM	0.3082	6058.00049	327.60016	95.7581

Figure 105. HPLC spectra of 2c



2c (The top one is racemic, and the bottom one is chiral)



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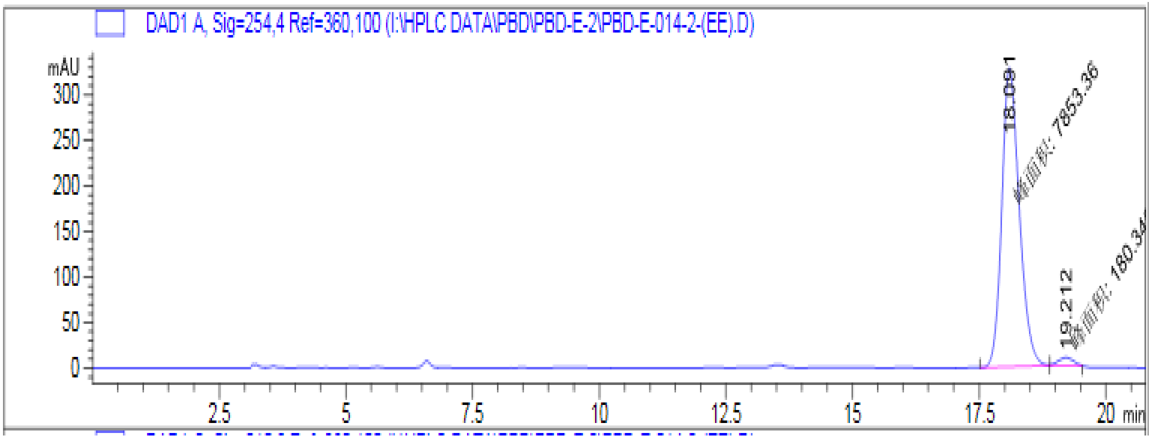
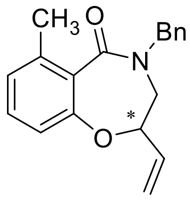
1	18.031	BV	0.3655	5786.64502	241.58044	50.0399
2	19.091	VB	0.4042	5777.41064	217.26256	49.9601

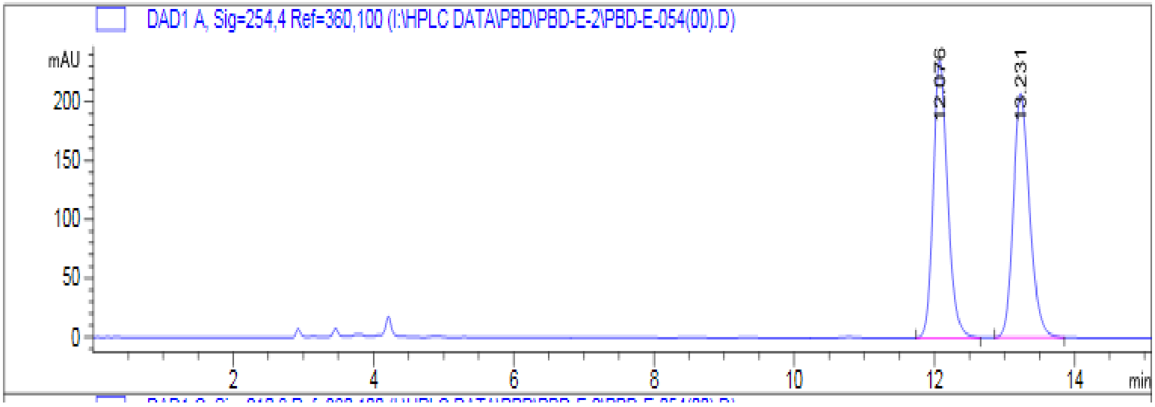


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	18.091	MM	0.3987	7853.35840	328.30087	97.7551
2	19.212	MM	0.3415	180.34630	8.80073	2.2449

Figure 106. HPLC spectra of 2d



2d (The top one is racemic, and the bottom one is chiral)



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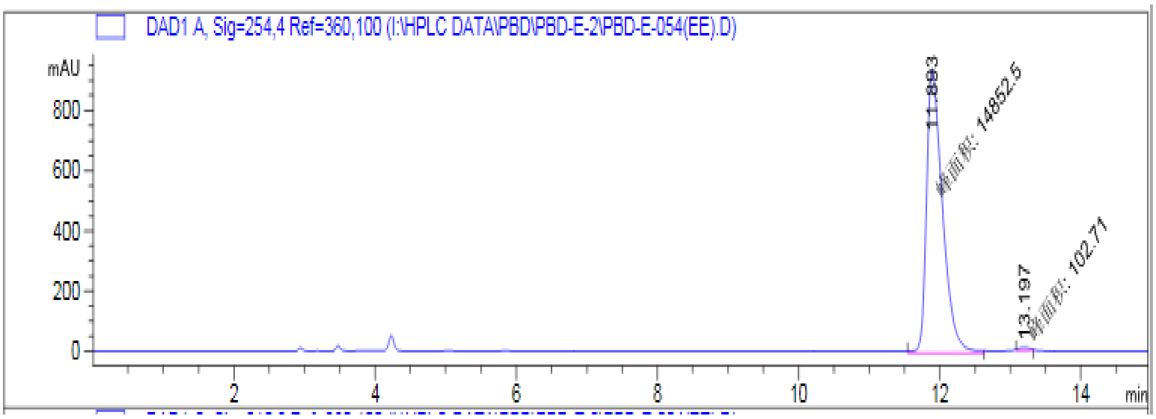
1	12.076	BB	0.2190	3379.71948	236.11810	50.0966
2	13.231	BB	0.2490	3366.67969	207.77133	49.9034



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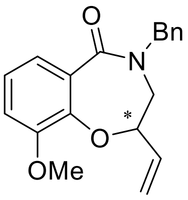
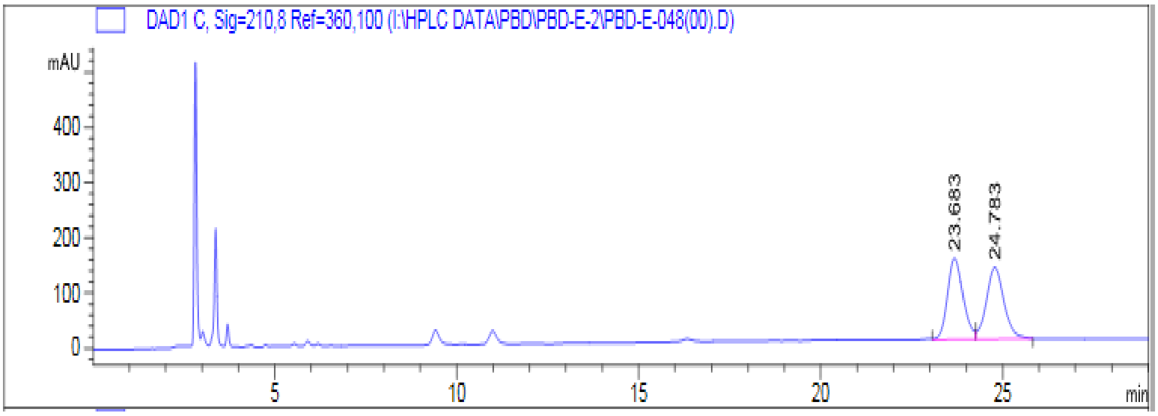
1	11.893	MM	0.2617	1.48525e4	945.82159	99.3132
2	13.197	MM	0.1785	102.71011	9.58746	0.6868

Figure 107. HPLC spectra of 2e



2e (The top one is racemic, and the bottom one is chiral)



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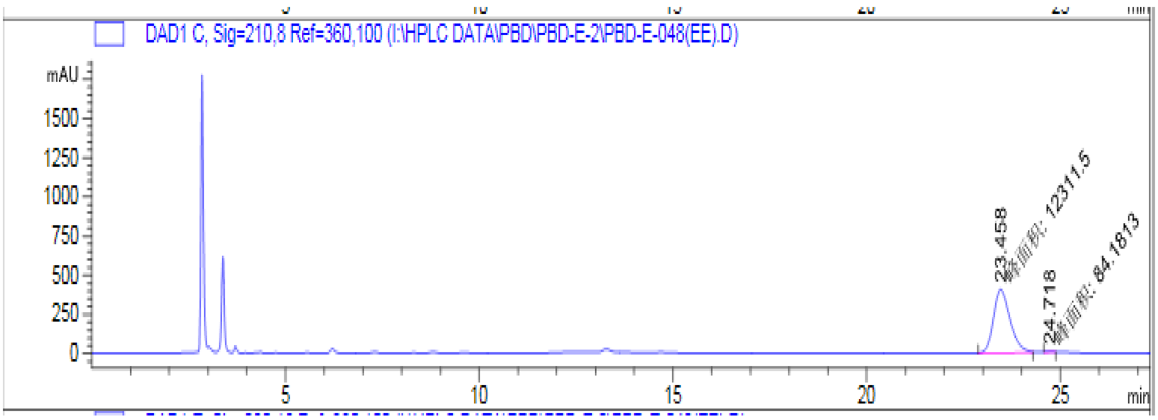
1	23.683	BV	0.4561	4359.03174	146.94899	49.7178
2	24.783	VB	0.5134	4408.52344	130.09148	50.2822



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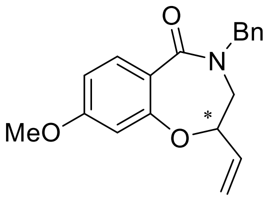
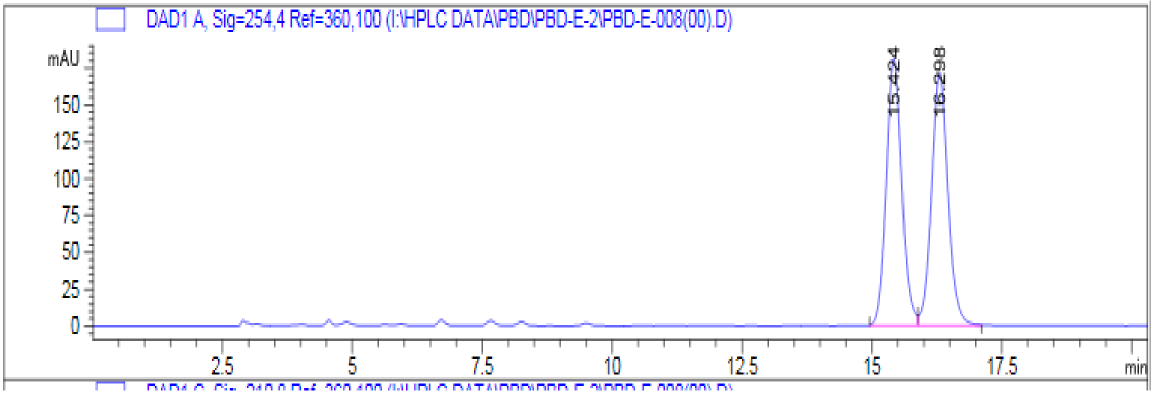
1	23.458	MM	0.5061	1.23115e4	405.41901	99.3209
2	24.718	MM	0.2665	84.18134	5.26373	0.6791

Figure 108. HPLC spectra of 2f



2f (The top one is racemic, and the bottom one is chiral)



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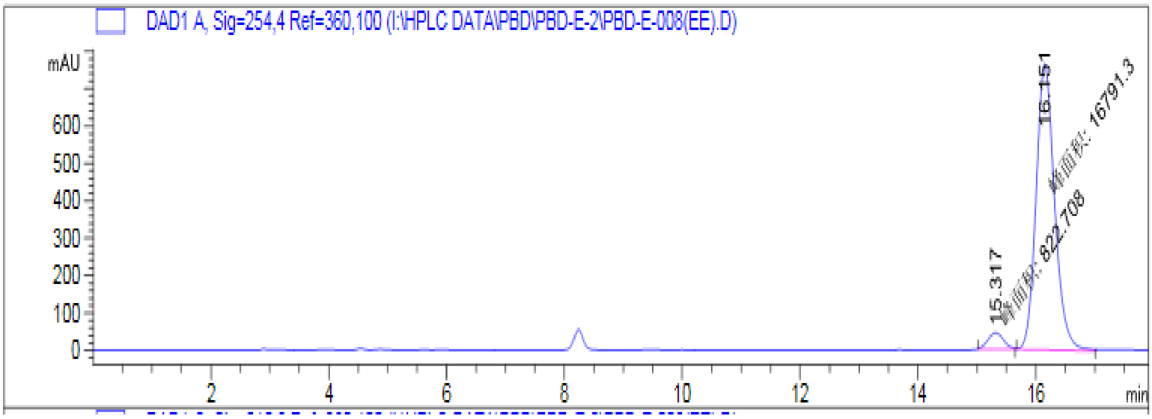
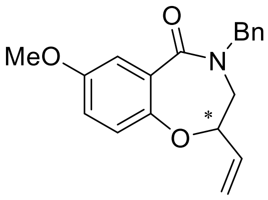
1	15.424	BV	0.3164	3727.25977	180.91608	49.6466
2	16.298	VB	0.3370	3780.31714	171.59616	50.3534

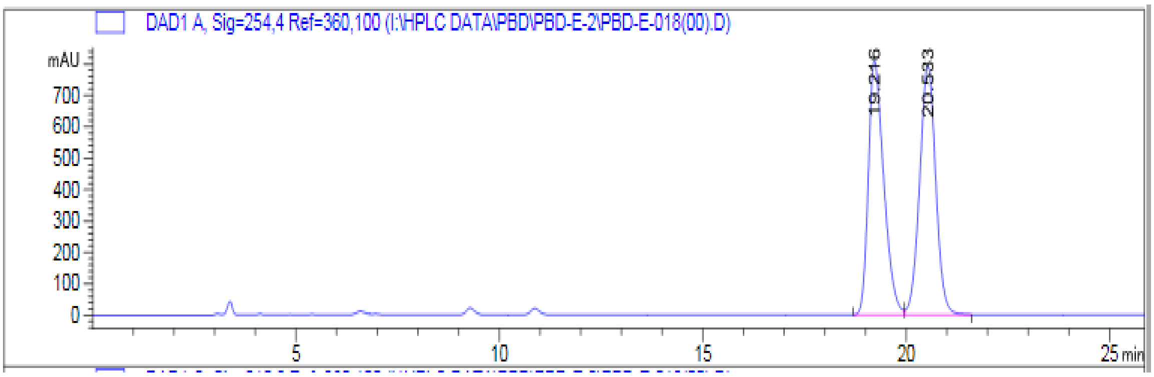


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.317	MM	0.3119	822.70837	43.95664	4.6708
2	16.151	MM	0.3650	1.67912e4	766.69623	95.3292

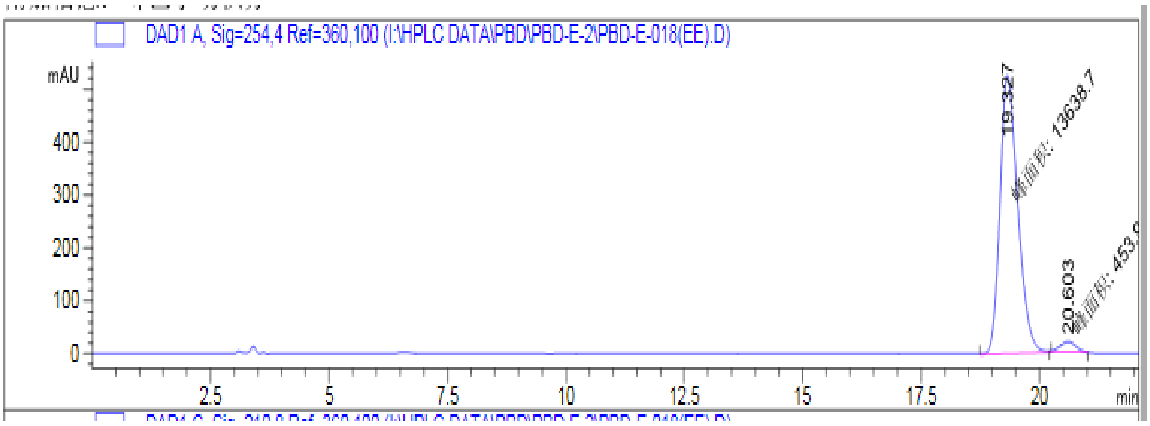
Figure 109. HPLC spectra of 2g



2g (The top one is racemic, and the bottom one is chiral)

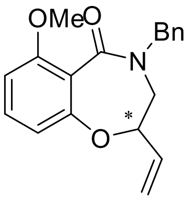


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	19.216	BV	0.3964	2.13216e4	811.85779	49.4274
2	20.533	VB	0.4248	2.18156e4	793.29089	50.5726

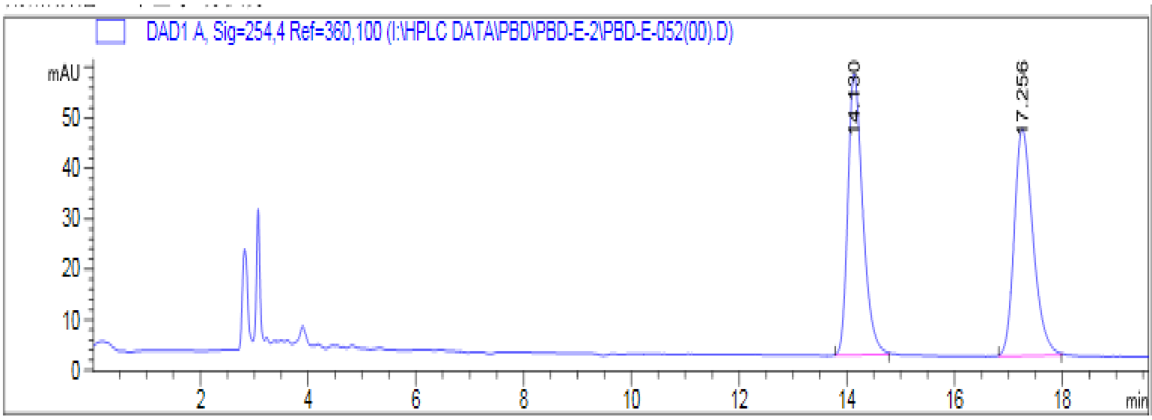


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	19.327	MM	0.4326	1.36387e4	525.45337	96.7786
2	20.603	MM	0.3822	453.98239	19.79851	3.2214

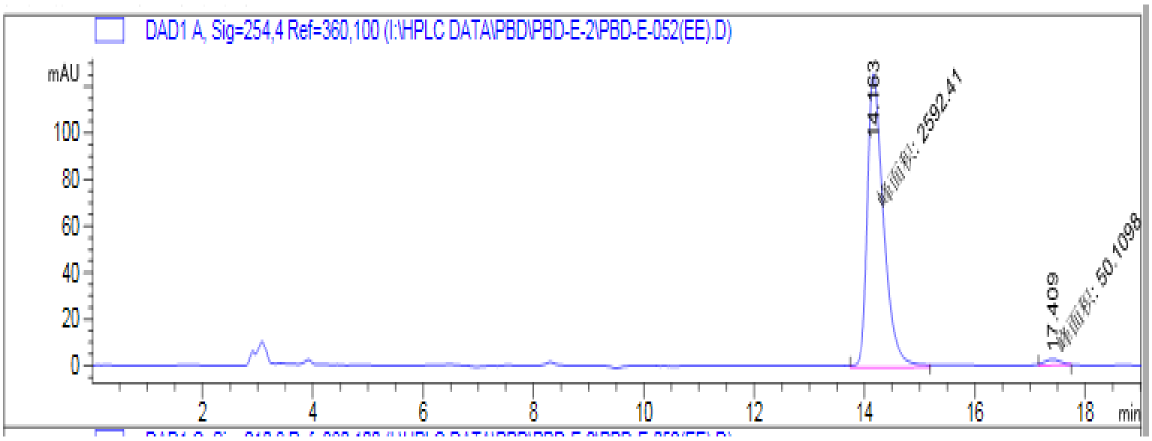
Figure 110. HPLC spectra of 2h



2h (The top one is racemic, and the bottom one is chiral)

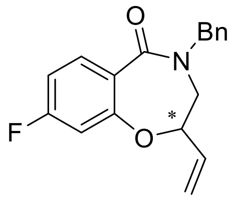


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	14.130	BB	0.2910	1077.04321	55.85306	49.5612
2	17.256	BB	0.3697	1096.11682	45.08308	50.4388

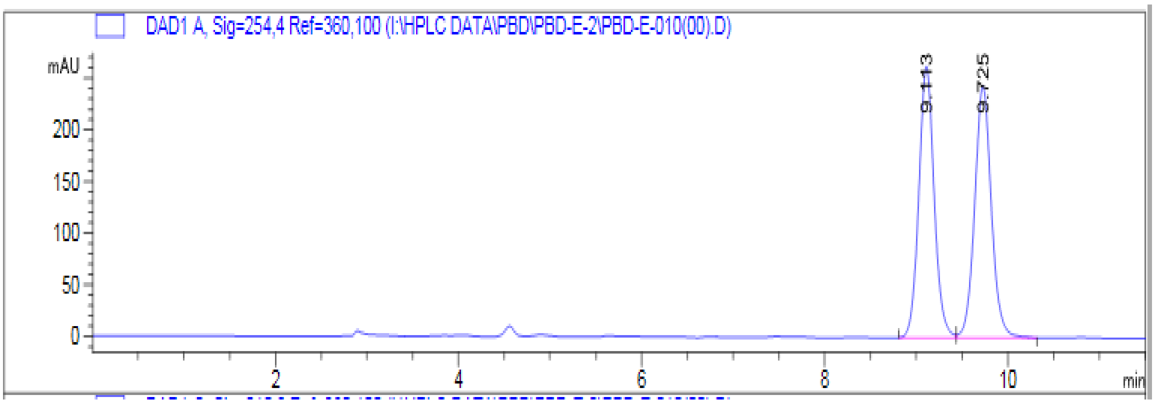


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	14.163	MM	0.3418	2592.40845	126.41183	98.1037
2	17.409	MM	0.3399	50.10984	2.45744	1.8963

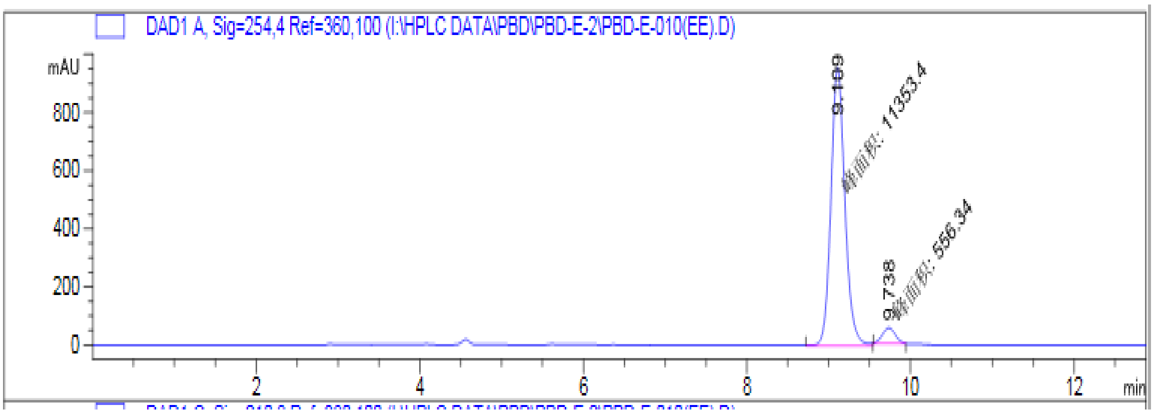
Figure 111. HPLC spectra of 2i



2i (The top one is racemic, and the bottom one is chiral)

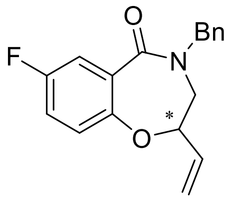


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.113	BV	0.1780	3067.32642	263.17606	49.7234
2	9.725	VB	0.1942	3101.44653	244.09389	50.2766

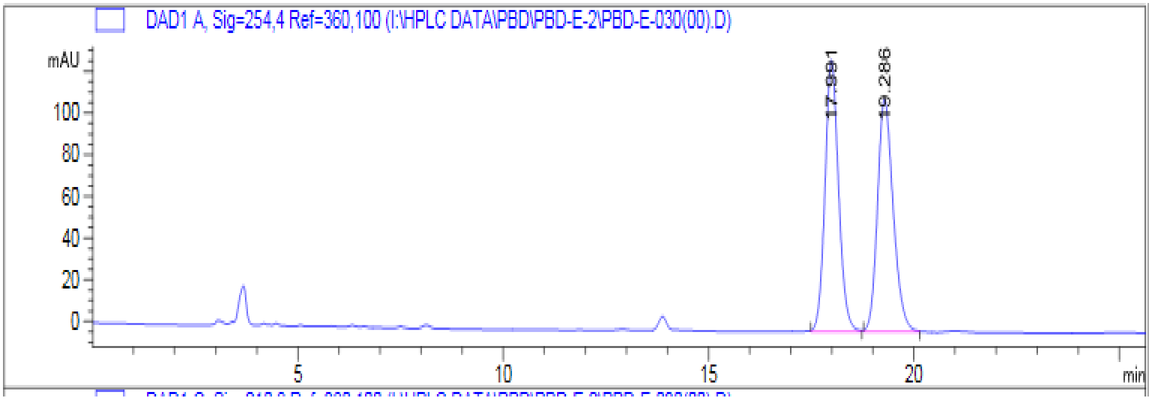


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.109	MM	0.1974	1.13534e4	958.51825	95.3287
2	9.738	MM	0.1791	556.34009	51.77598	4.6713

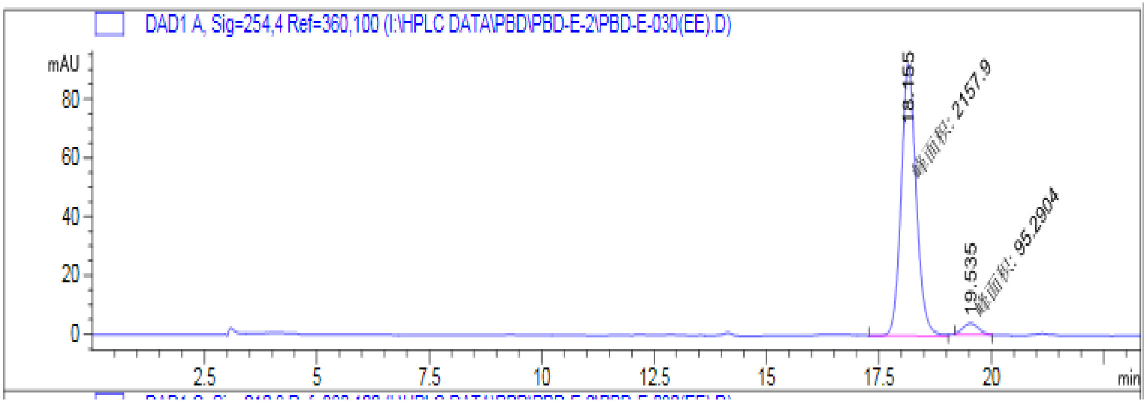
Figure 112. HPLC spectra of 2j



2j (The top one is racemic, and the bottom one is chiral)

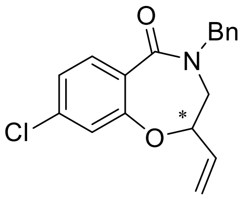


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	17.991	BB	0.3496	2984.93042	130.12889	50.0440
2	19.286	BB	0.4056	2979.68286	111.57561	49.9560

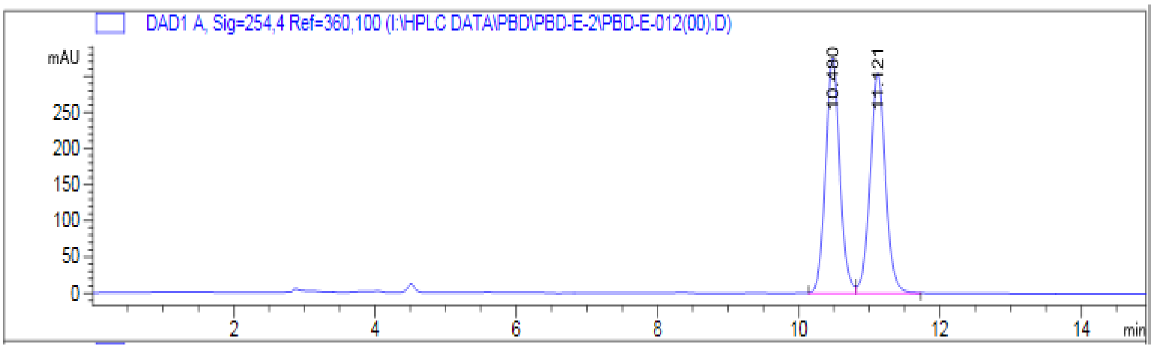


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	18.155	MM	0.3887	2157.89600	92.53067	95.7709
2	19.535	MM	0.4026	95.29037	3.94457	4.2291

Figure 113. HPLC spectra of 2k

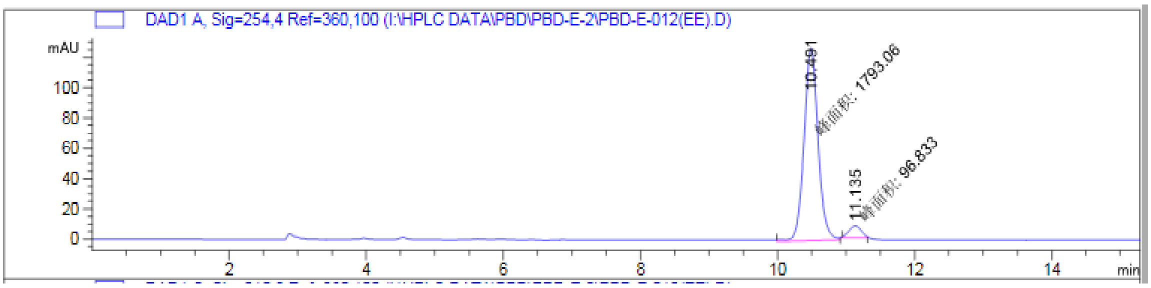


2k (The top one is racemic, and the bottom one is chiral)



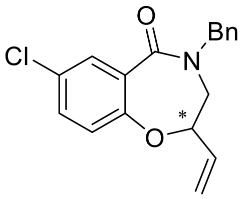
信号 1: DAD1 A, Sig=254,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.480	BV	0.2133	4558.25049	325.57504	49.8014
2	11.121	VB	0.2304	4594.60596	303.84317	50.1986

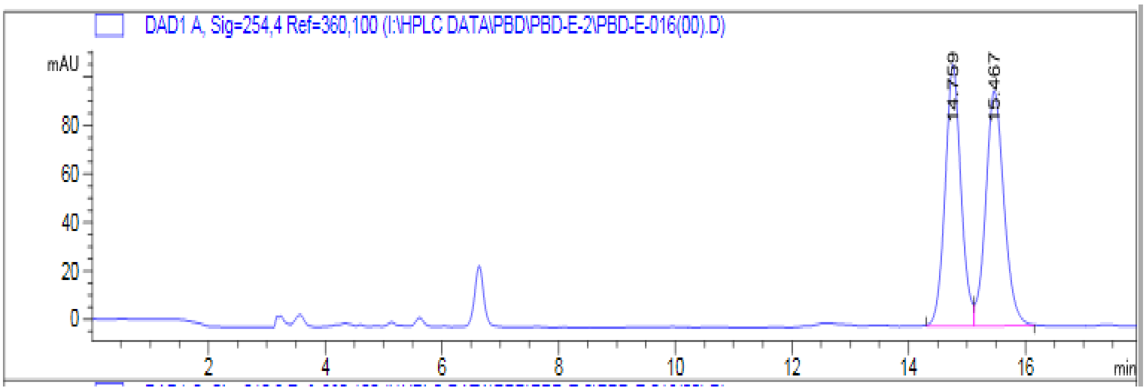


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.491	MM	0.2353	1793.05981	127.00144	94.8763
2	11.135	MM	0.2074	96.83298	7.78169	5.1237

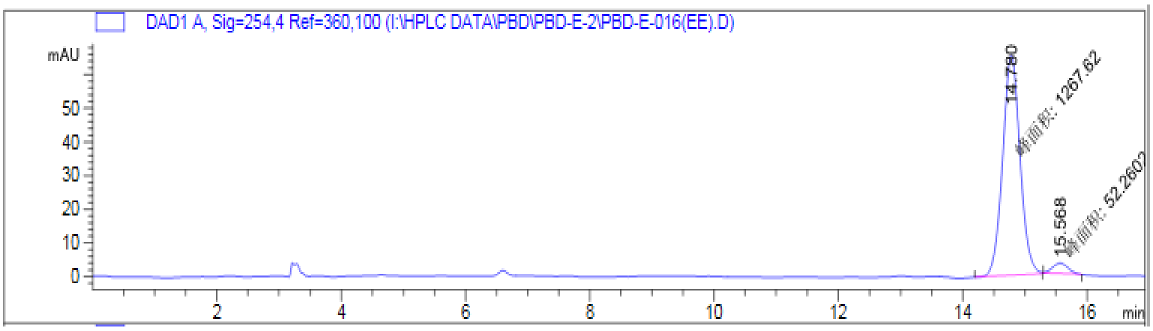
Figure 114. HPLC spectra of 2l



2l (The top one is racemic, and the bottom one is chiral)

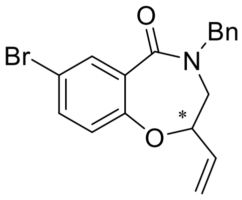


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	14.759	BV	0.2919	2069.95288	107.87402	49.6756
2	15.467	VB	0.3288	2096.98657	96.77274	50.3244

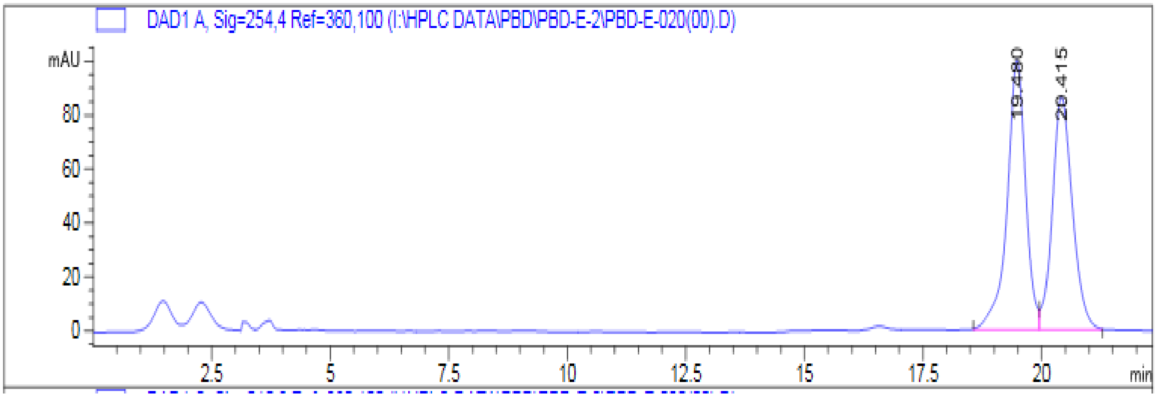


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	14.780	MM	0.3231	1267.62146	65.38344	96.0405
2	15.568	MM	0.2854	52.26015	3.05154	3.9595

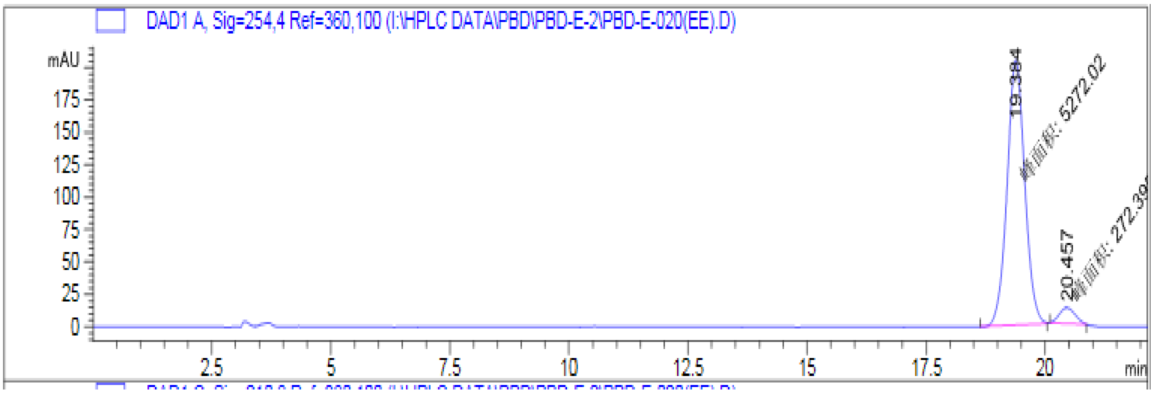
Figure 115. HPLC spectra of 2m



2m (The top one is racemic, and the bottom one is chiral)

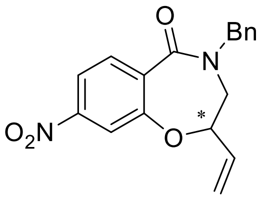


峰 \#	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	19.480	BV	0.4094	2741.20361	100.12223	51.7716
2	20.415	VB	0.4460	2553.60034	86.61641	48.2284

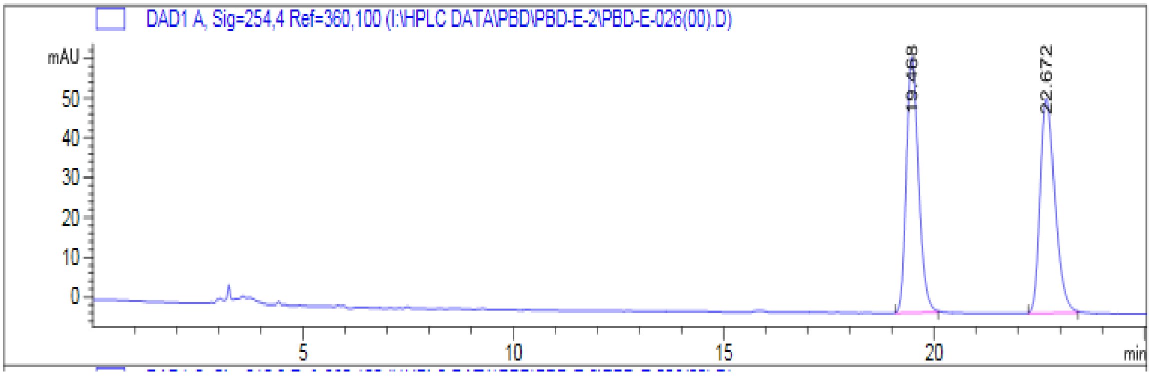


峰 \#	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	19.384	MM	0.4299	5272.02148	204.41234	95.0870
2	20.457	MM	0.3761	272.39450	12.07028	4.9130

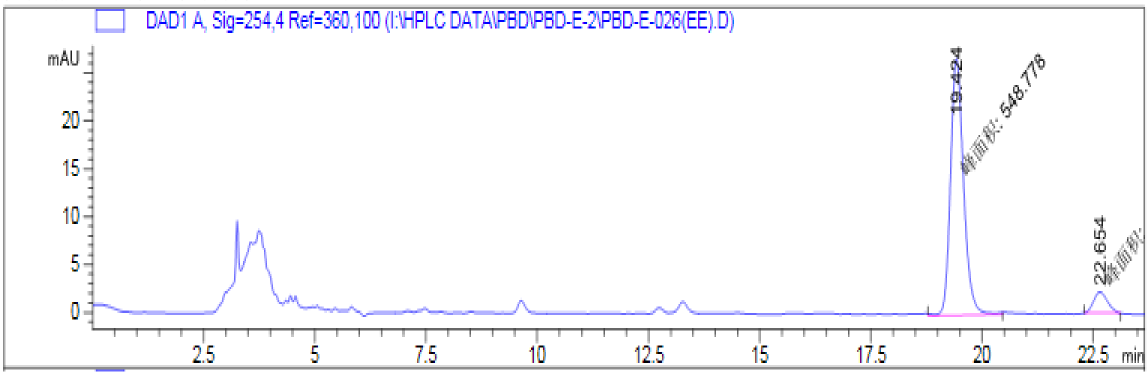
Figure 116. HPLC spectra of 2n



2n (The top one is racemic, and the bottom one is chiral)

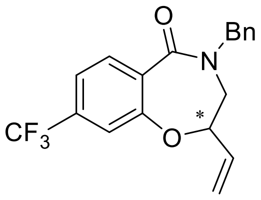


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	19.468	BB	0.3119	1302.02173	64.38039	49.9371
2	22.672	BB	0.3729	1305.30127	53.83696	50.0629

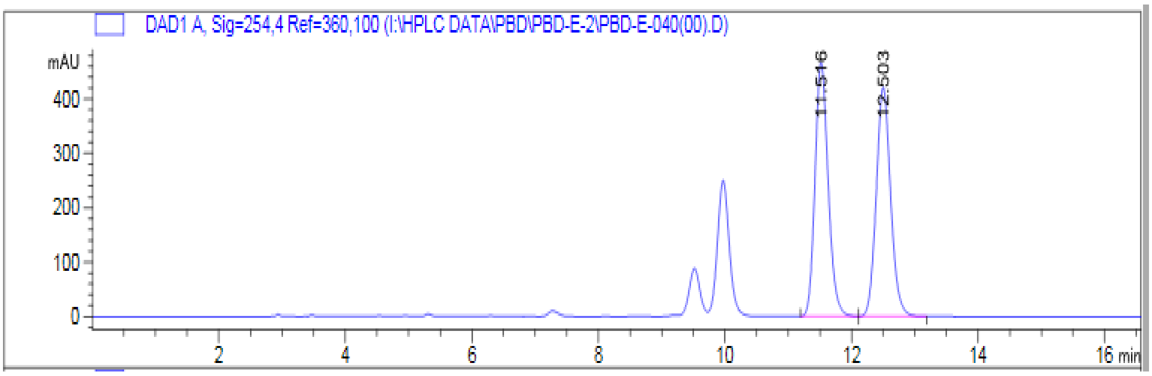


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	19.424	MM	0.3414	548.77795	26.79387	92.1054
2	22.654	MM	0.3590	47.03728	2.18365	7.8946

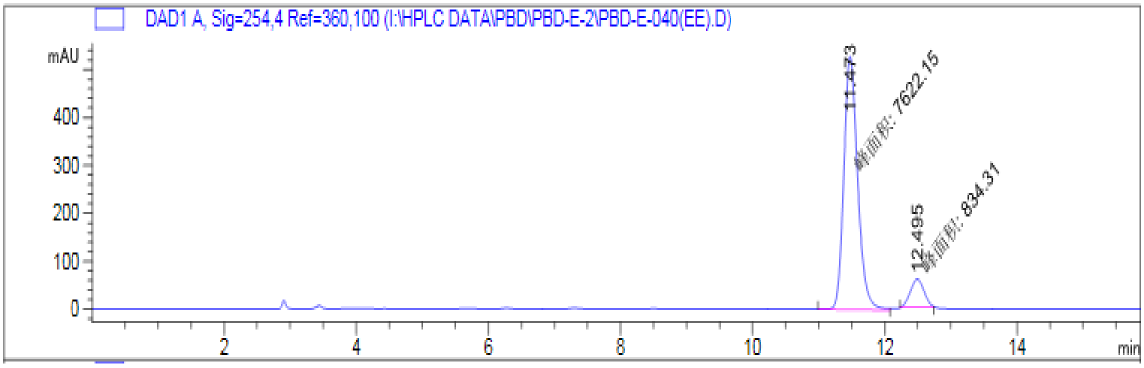
Figure 117. HPLC spectra of 2o



2o (The top one is racemic, and the bottom one is chiral)

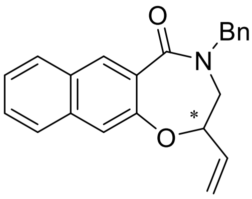


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.516	BV	0.2220	6730.11670	467.24707	50.3815
2	12.503	VB	0.2416	6628.18408	421.16309	49.6185

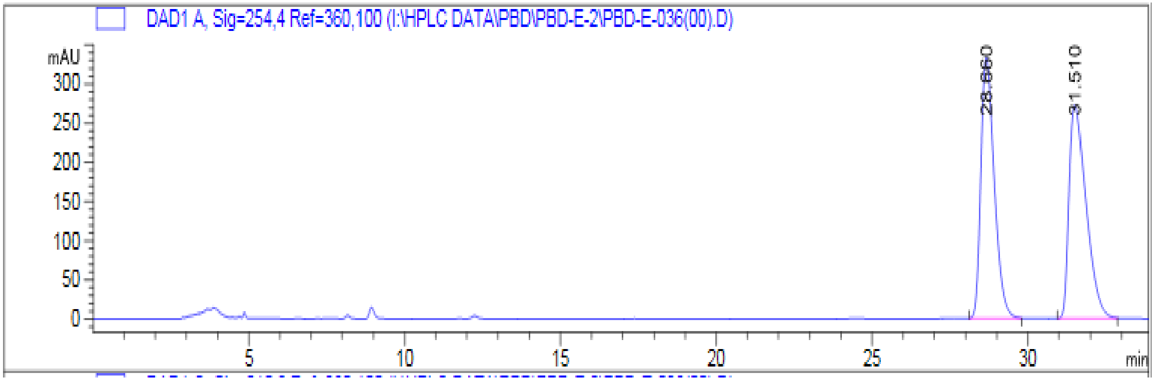


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.473	MM	0.2402	7622.15479	528.91931	90.1341
2	12.495	MM	0.2388	834.30988	58.24003	9.8659

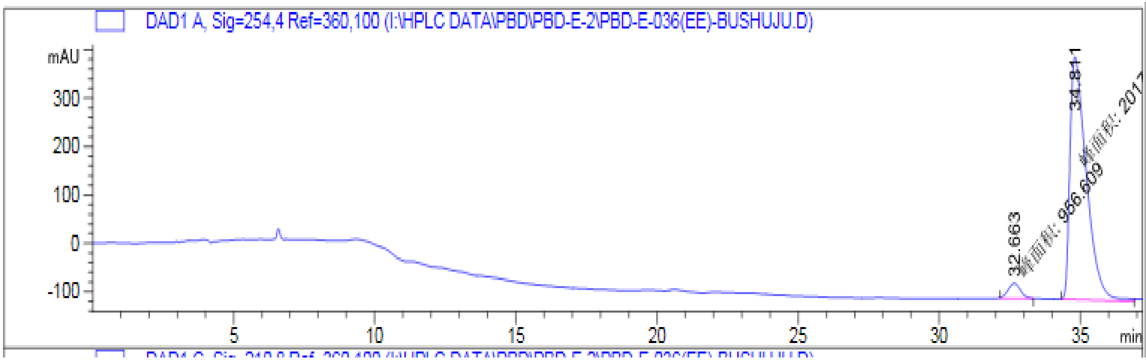
Figure 118. HPLC spectra of 2p



2p (The top one is racemic, and the bottom one is chiral)

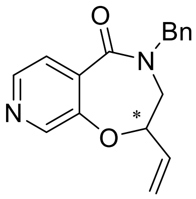


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	28.660	BB	0.4598	1.00025e4	333.56821	49.4918
2	31.510	BB	0.5779	1.02079e4	271.98752	50.5082

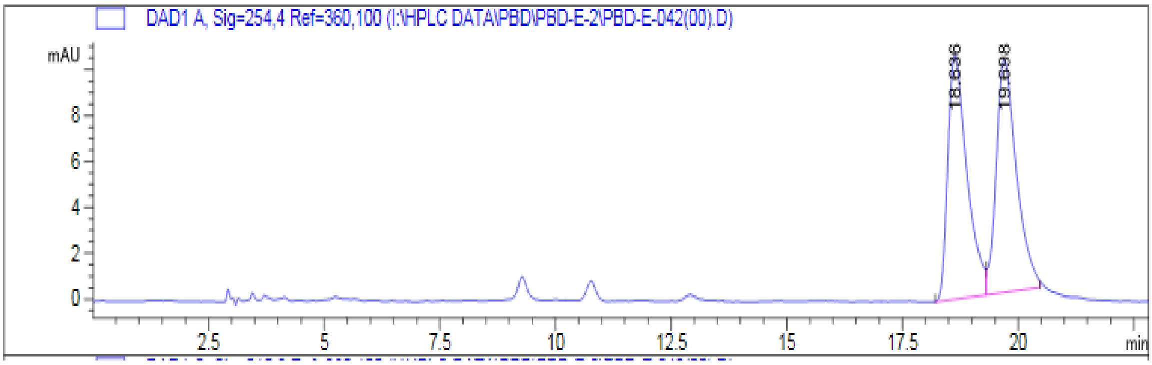


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	32.663	MM	0.5075	956.60858	31.41396	4.5264
2	34.811	MM	0.6713	2.01772e4	500.94193	95.4736

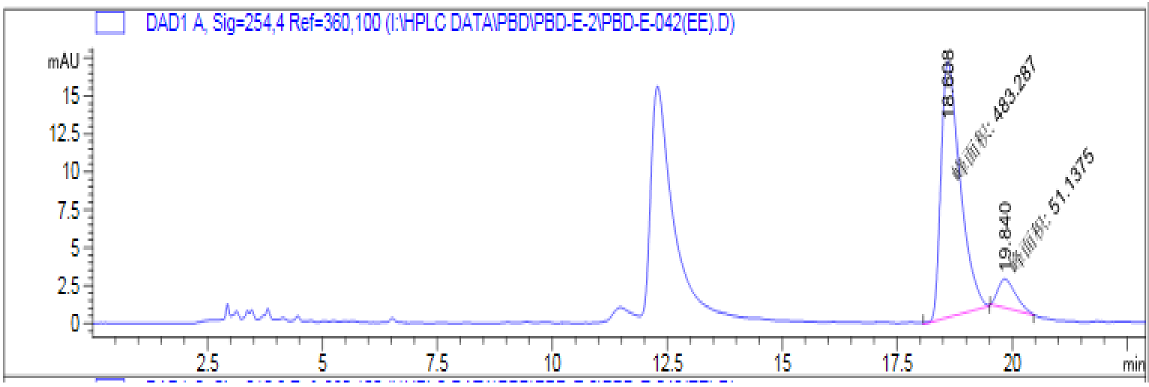
Figure 119. HPLC spectra of 2q



2q (The top one is racemic, and the bottom one is chiral)

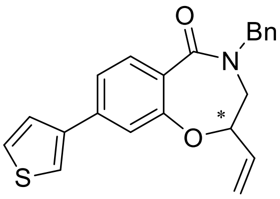


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	18.636	BV	0.4283	306.29074	10.62653	49.6421
2	19.698	VB	0.4469	310.70764	10.15777	50.3579

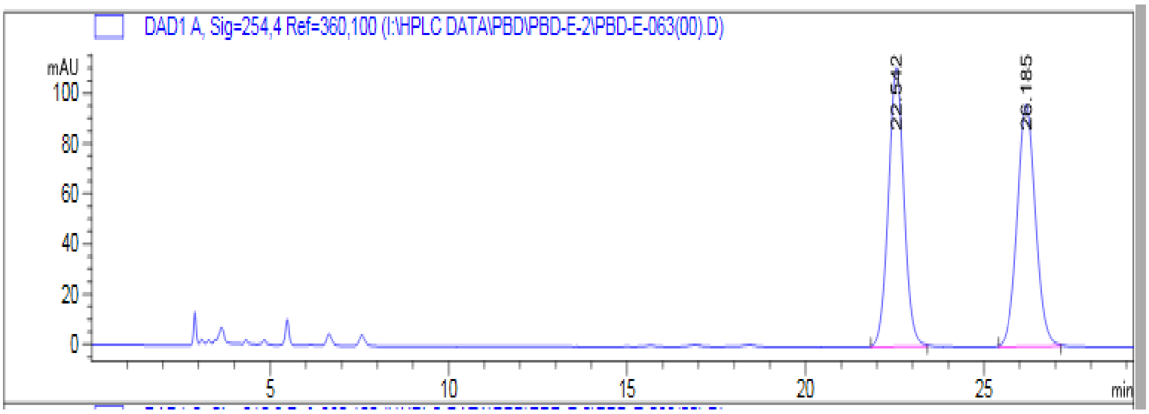


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	18.608	MM	0.4771	483.28738	16.88255	90.4313
2	19.840	MM	0.4534	51.13749	1.87995	9.5687

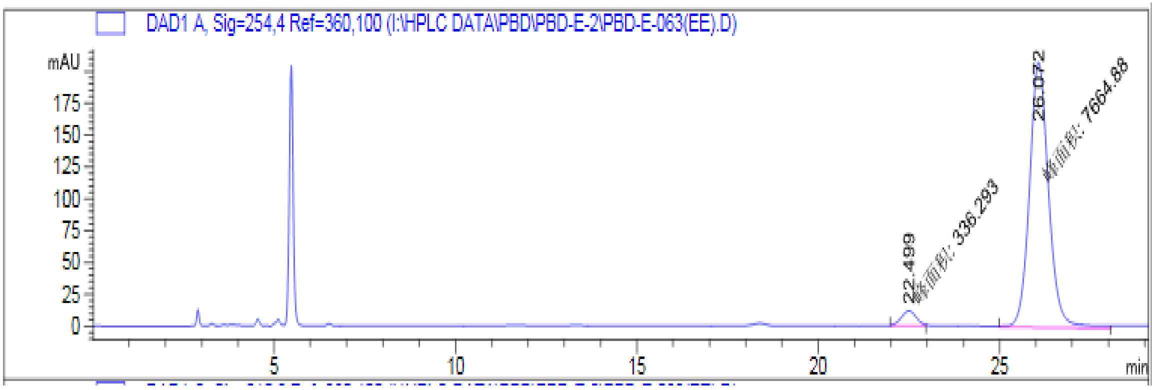
Figure 120. HPLC spectra of 2r



2r (The top one is racemic, and the bottom one is chiral)

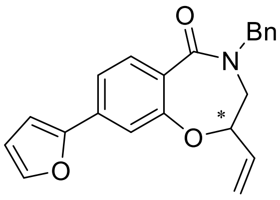


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	22.542	BB	0.4735	3423.20728	111.08373	49.9619
2	26.185	BB	0.5448	3428.42285	96.43333	50.0381

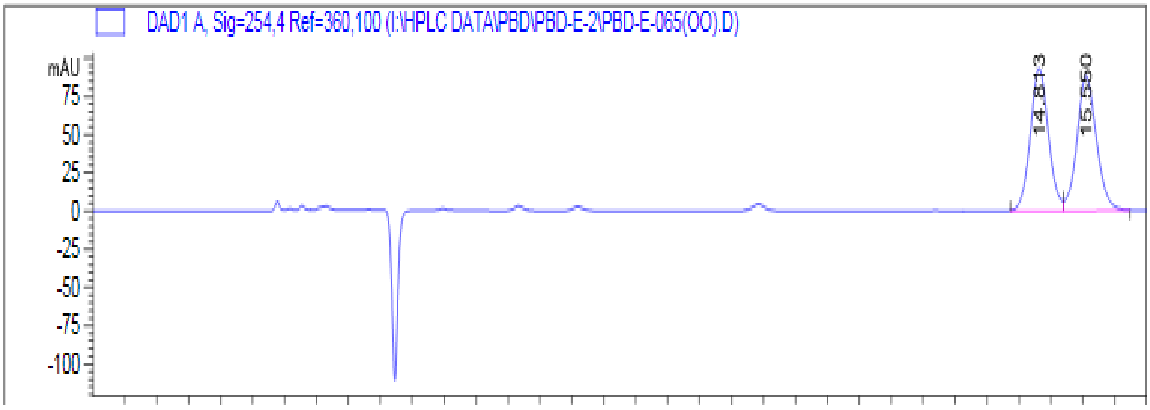


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	22.499	MM	0.4826	336.29303	11.61428	4.2030
2	26.072	MM	0.6147	7664.88232	207.83022	95.7970

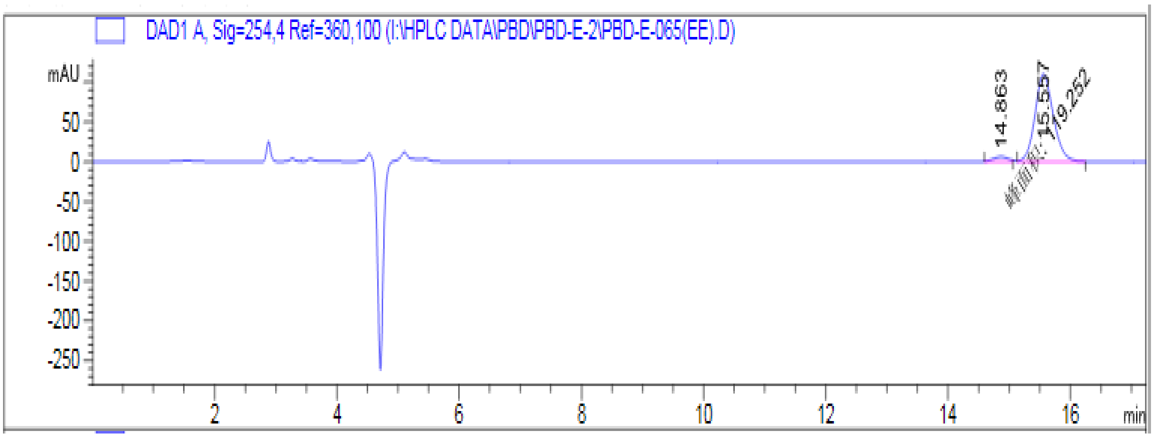
Figure 121. HPLC spectra of 2s



2s (The top one is racemic, and the bottom one is chiral)

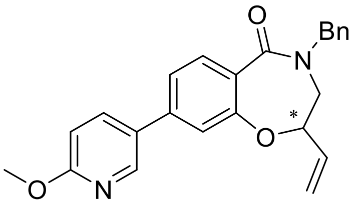


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	14.813	BV	0.2999	1839.17896	93.32905	49.5029
2	15.550	VB	0.3229	1876.12012	87.93398	50.4971

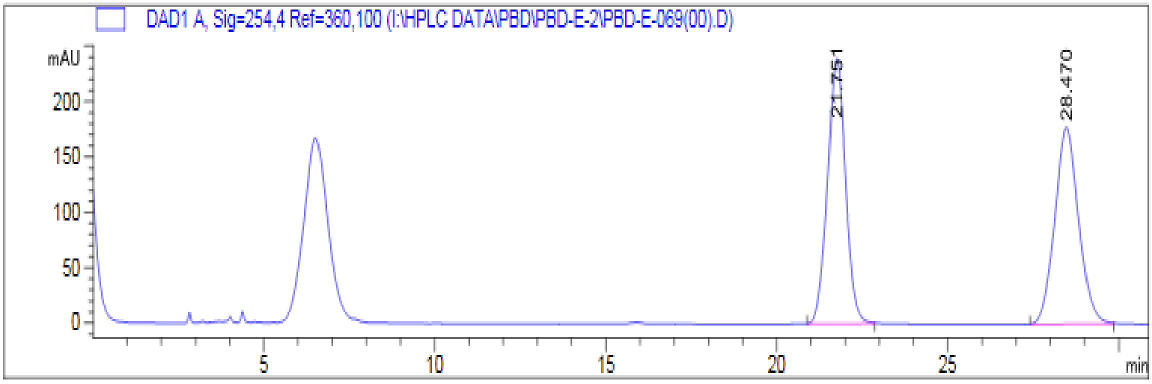


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	14.863	MM	0.3010	119.25154	6.60352	4.9006
2	15.557	VB	0.3189	2314.14966	110.23541	95.0994

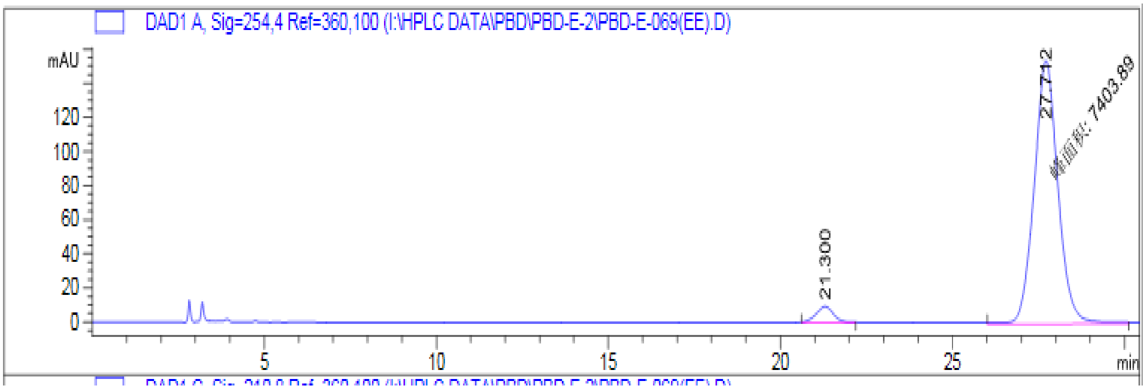
Figure 122. HPLC spectra of 2t



2t (The top one is racemic, and the bottom one is chiral)

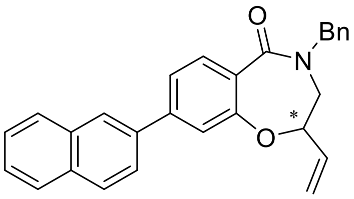


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	21.751	BB	0.5465	8680.01563	239.67952	50.1891
2	28.470	BB	0.7197	8614.59961	177.65236	49.8109

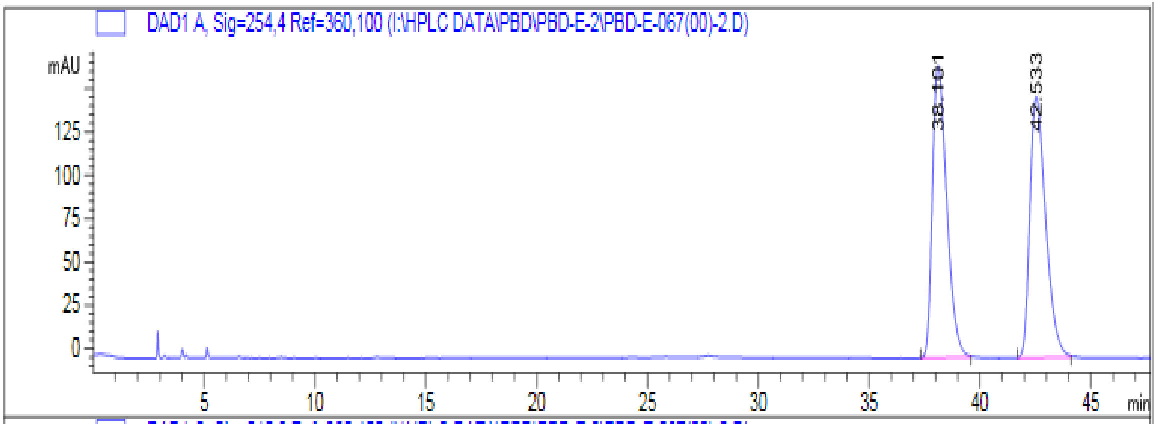


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	21.300	BB	0.5340	327.78497	9.32783	4.2395
2	27.712	MM	0.7992	7403.88672	154.40346	95.7605

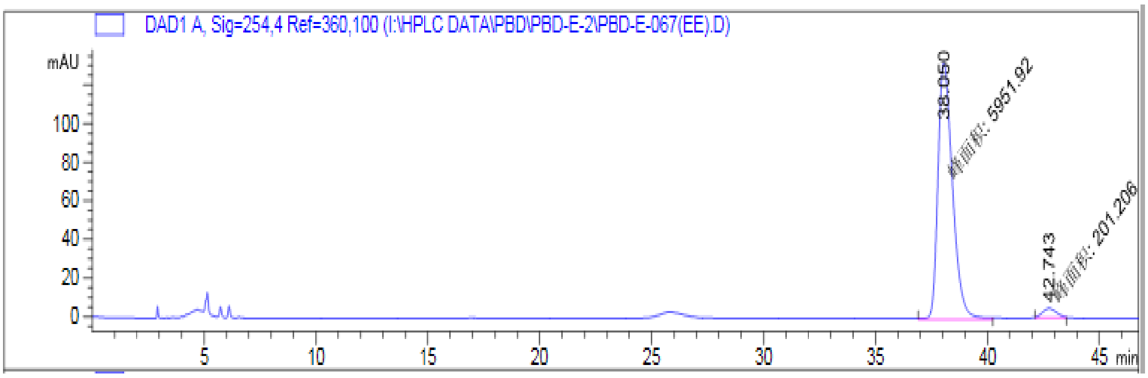
Figure 123. HPLC spectra of 2u



2u (The top one is racemic, and the bottom one is chiral)

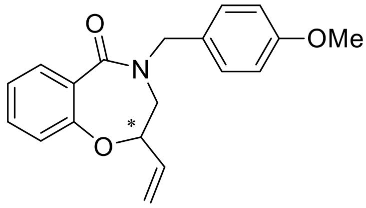


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	38.101	BB	0.6993	7579.92383	168.34131	50.3421
2	42.533	BB	0.7598	7476.89844	150.45316	49.6579

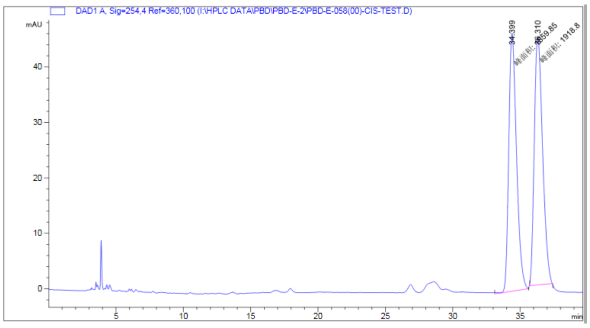


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	38.050	MM	0.7458	5951.92285	133.00870	96.7300
2	42.743	MM	0.7078	201.20631	4.73791	3.2700

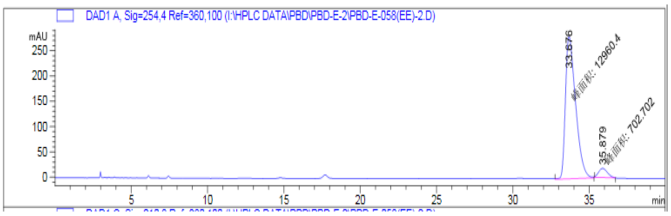
Figure 124. HPLC spectra of 2v



2v (The top one is racemic, and the bottom two are chiral)



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	34.399	MM	0.6661	1859.84827	46.53275	49.2199
2	36.310	MM	0.7139	1918.80212	44.79788	50.7801

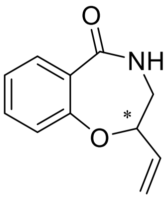


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	33.676	MM	0.7690	1.29604e4	280.88150	94.8570
2	35.879	MM	0.6541	702.70227	17.90641	5.1430

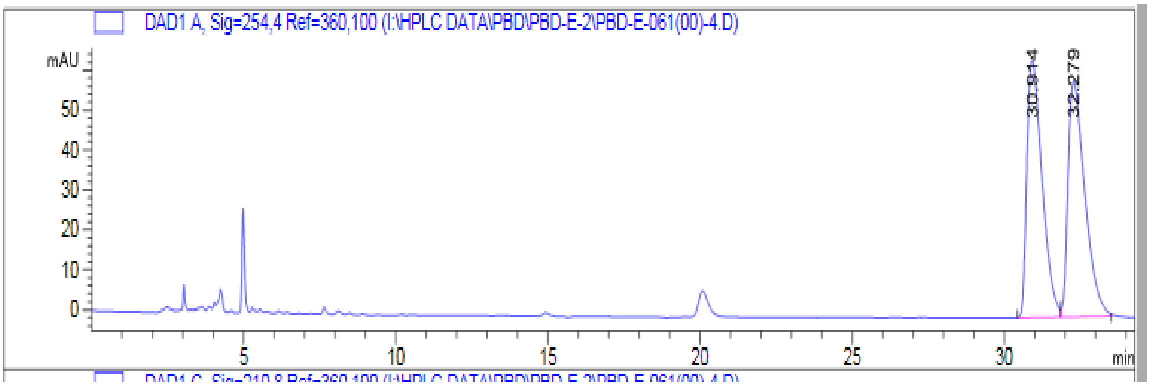
This one is prepared from cis-substrate (*Z*-1v).

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	34.931	MM	0.6271	1085.71582	28.85613	13.5556
2	36.551	MM	0.8102	6923.62500	142.43466	86.4444

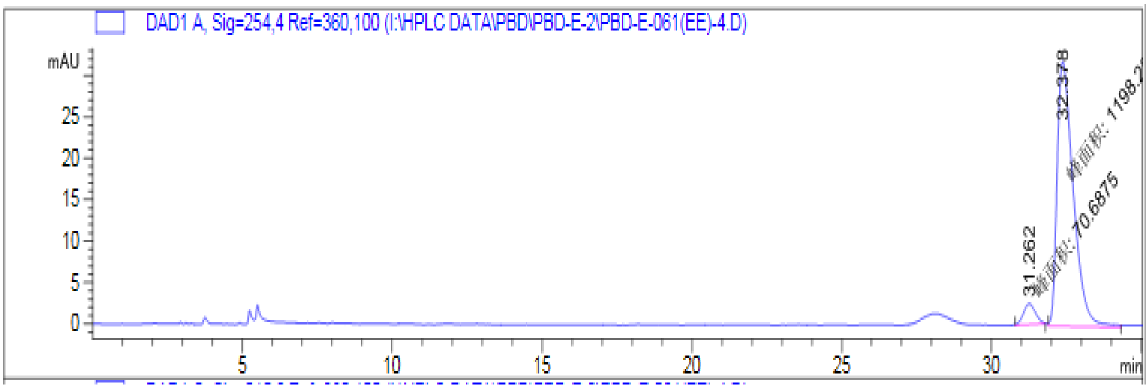
Figure 125. HPLC spectra of 3v



3v (The top one is racemic, and the bottom one is chiral)

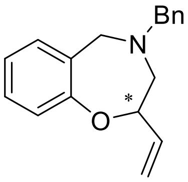


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	30.914	BV	0.5304	2232.65527	64.41662	49.7538
2	32.279	VB	0.5785	2254.75366	58.91465	50.2462

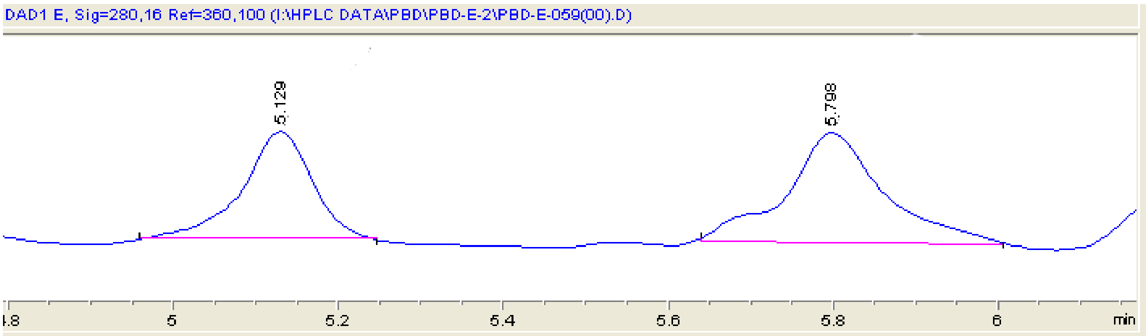


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	31.262	MM	0.4681	70.68752	2.51670	5.5705
2	32.378	MM	0.6247	1198.28235	31.96801	94.4295

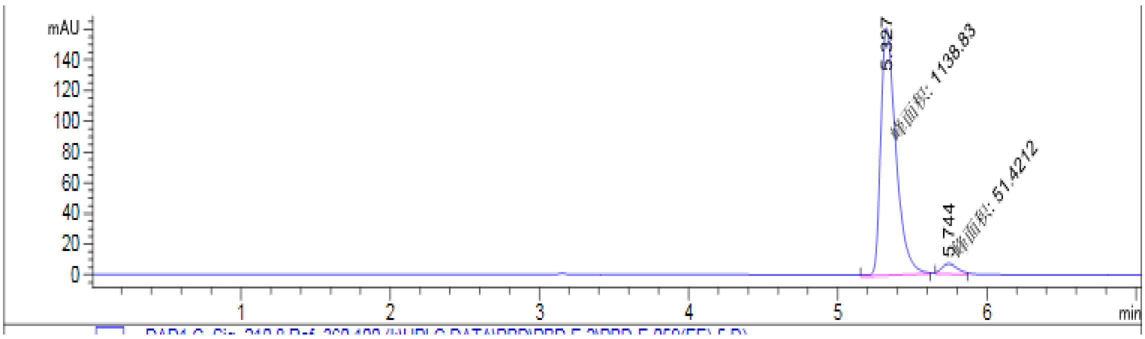
Figure 126. HPLC spectra of 3a



3a (The top one is racemic, and the bottom one is chiral)

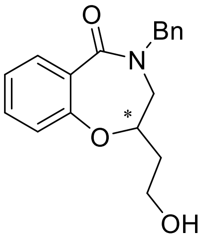


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	5.130	MM	0.1059	17.85892	2.81030	50.0711
2	5.798	MM	0.1181	17.80818	2.51357	49.9289

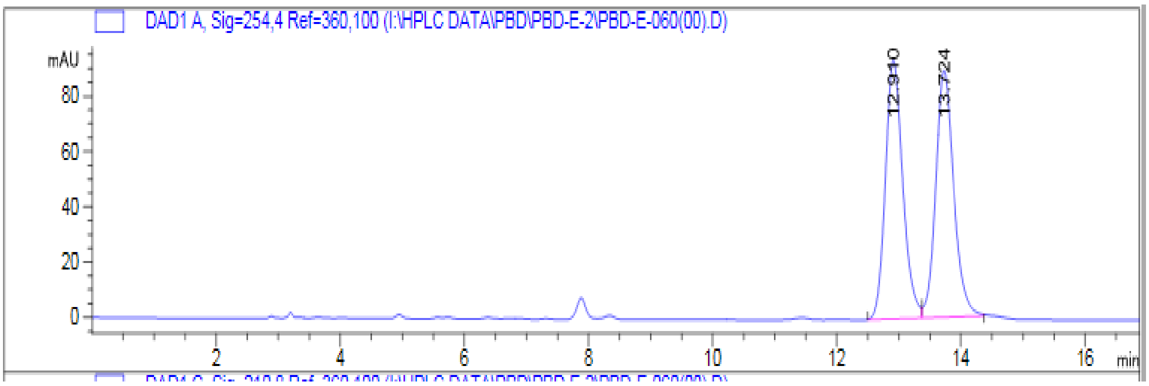


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	5.327	MM	0.1174	1138.82593	161.69975	95.6798
2	5.744	MM	0.1240	51.42119	6.90924	4.3202

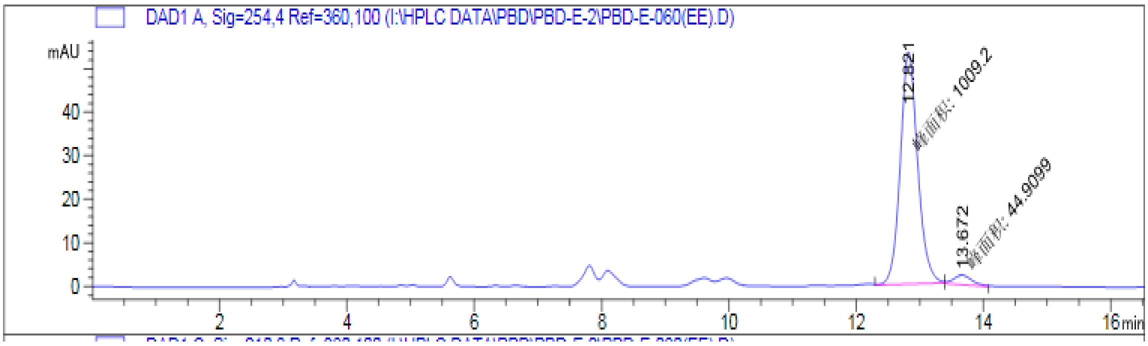
Figure 127. HPLC spectra of 4a



4a (The top one is racemic, and the bottom one is chiral)



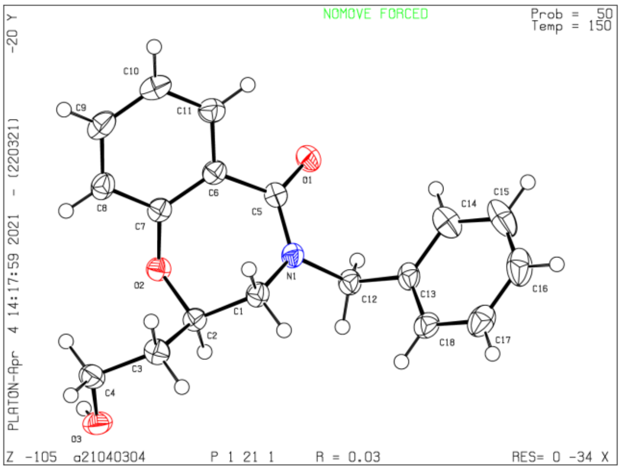
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	12.910	BV	0.2960	1813.84961	93.63516	49.9712
2	13.724	VB	0.3094	1815.94397	89.25263	50.0288



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	12.821	MM	0.3156	1009.19513	53.29708	95.7395
2	13.672	MM	0.3375	44.90985	2.21809	4.2605

6. X-ray Crystallogaphic Data

Figure 128. X-Ray Crystallographic Data for Compound(*R*)-4a



Structure factors have been supplied for datablock(s) (CCDC: 2076650)

Bond precision:	C-C = 0.0025 A		Wavelength=1.54184
Cell:	a=7.90381(18)	b=8.25775(16)	c=12.5469(3)
	alpha=90	beta=108.190(3)	gamma=90
Temperature:	150 K		

	Calculated	Reported
Volume	777.98(3)	777.98(3)
Space group	P 21	P 1 21 1
Hall group	P 2yb	P 2yb
Moiety formula	C18 H19 N O3	C18 H19 N O3
Sum formula	C18 H19 N O3	C18 H19 N O3
Mr	297.34	297.34
Dx,g cm-3	1.269	1.269
Z	2	2
Mu (mm-1)	0.698	0.698
F000	316.0	316.0
F000’	316.96	
h,k,lmax	9,10,15	9,10,15
Nref	3247[1738]	2225
Tmin,Tmax	0.935,0.966	0.954,1.000
Tmin’	0.864	

Correction method= # Reported T Limits: Tmin=0.954 Tmax=1.000

AbsCorr = MULTI-SCAN

Data completeness= 1.28/0.69	Theta(max)= 75.960
R(reflections)= 0.0278(2186)	wR2(reflections)= 0.0722(2225)
S = 1.064	Npar= 201